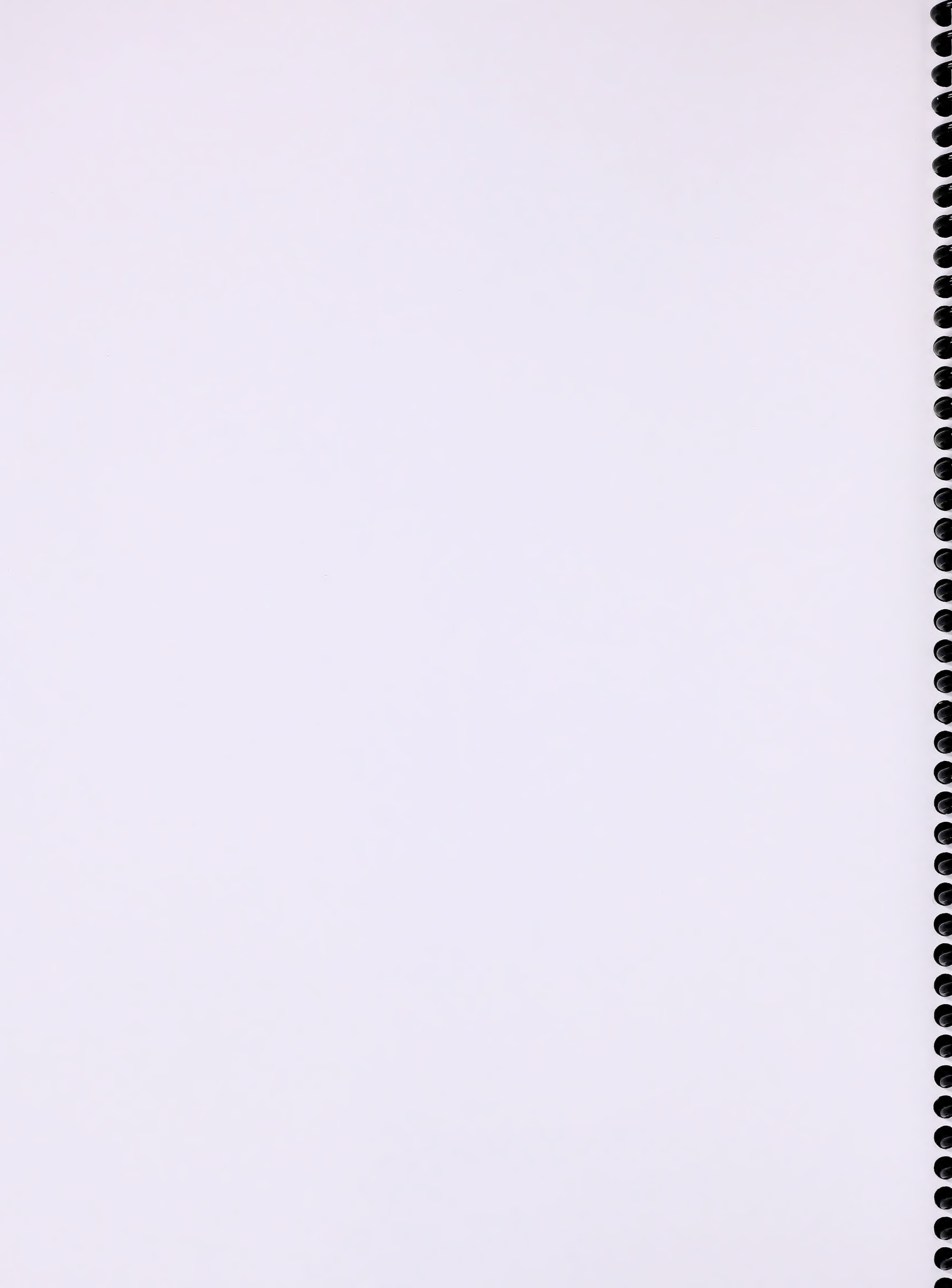


# **Review and Assessment of Methods for Monitoring and Estimating Dry Deposition in Alberta**





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Alberta Environment  
Edmonton, Alberta**

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**By:  
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St Albert, Alberta**

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## FOREWORD

Acid deposition occurs when acidifying pollutants emitted from anthropogenic and other processes undergo chemical reactions in the atmosphere and fall to the earth as wet deposition (rain, snow, cloud, fog) or dry deposition (dry particles, gas). Acidic pollutants can be transported long distances in the atmosphere from their sources and eventually be deposited in ecosystems over broad regional scales and in locations far from the emission sources.

Dry deposition is generally more a local problem than wet deposition. Direct measurement of dry deposition rates is difficult. Dry deposition depends on many factors, including: meteorological conditions, characteristics of the pollutants being deposited (e.g. different gaseous chemical and particle size), and characteristics of the surface on which deposition occurs.

The most accepted and common method for estimating dry deposition is the so-called “inference method.” The inferential method is a combination of measurement and modeling that involves indirect estimation of dry deposition rates on the basis of routinely measured air concentrations and meteorological parameters. The method is based on an assumed steady-state relationship  $F = V_d C$ , where the dry deposition flux or rate ( $F$ ) is a product of the dry deposition velocity ( $V_d$ ) and the concentration ( $C$ ) of an airborne pollutant.

A series of studies have been initiated by AENV to evaluate the inference method and search for the most suitable and simple model for deposition rate estimations in Alberta. This report documents the first study in the series. Titles for the reports of the other studies are: “*Dry Deposition Monitoring Method in Alberta*”, and “*Refinement Study of Dry Deposition Inference Method Used in Alberta*”. It is anticipated that once all necessary information is gathered, an Alberta protocol for dry deposition measurement will be prepared.

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## EXECUTIVE SUMMARY

Acid deposition occurs when acidifying pollutants emitted from anthropogenic and other processes undergo complex chemical reactions in the atmosphere and fall to the earth as wet deposition (rain, snow, cloud, fog) or dry deposition (dry particles, gas). The main chemical precursors leading to acidic pollutants are atmospheric concentrations of sulphur dioxide ( $\text{SO}_2$ ) and oxides of nitrogen ( $\text{NO}_x$ ). Direct monitoring of dry deposition at the earth's surface is not possible at this time. Instead monitoring of ambient concentrations of acidifying substances in air is used. Estimation of dry deposition is then based upon these ambient measurements multiplied by a deposition velocity for each substance.

Currently there is no standard method for the field measurement and estimation of dry deposition of acidifying pollutants released into the environment. The objectives of this study were to examine current approaches used for measuring and estimating dry deposition and to identify whether a relatively economical technical approach can be put into practice for measuring and estimating dry deposition of acidic substances across airsheds in Alberta. The following findings are noted:

1. Components of a dry deposition network in the presence of multiple important emitting sources within a region should include:
  - Dedicated monitoring at a site to capture representative local influences of N and S species deposition.
  - Dedicated monitoring at a site representing lower N and S species deposition than what would exist near important source emitting areas.
  - Information on spatial variation of N and S species deposition within a region using less-expensive passive monitors. This approach will admittedly introduce uncertainty into dry deposition estimates as selected acidic parameters would not be monitored. However a tradeoff is being made in costs for obtaining information on dry deposition for at least some acidic parameters (e.g.  $\text{SO}_2$ ,  $\text{NO}_2$ ).
2. Passive monitoring of  $\text{HNO}_3$  and  $\text{HNO}_2$  has been recently developed and used in warmer climates. If such an approach were to be considered in Alberta, field testing would be required to calibrate the monitors against a reference method to better understand the monitoring capabilities in cold climates.
3. As most dry deposition monitoring is currently undertaken by airshed organizations in Alberta, it makes sense to present these organizations with an approach that is practical, reasonably cost-effective, and takes into account site-specific information needs. With this in mind, these organizations should make better attempts at standardizing their monitoring procedures in terms of frequency and duration for both acidic parameters and meteorological parameters. The opportunity exists to develop a more formal network for monitoring dry deposition in Alberta airsheds that places greater emphasis on using consistent procedures for measuring and calculating dry deposition of acidic parameters. Specifically, this relates to:
  - The type of acidic and meteorological parameters to measure.
  - The frequency and duration in which the selected parameters are measured.



- The quantitative relationships and corresponding assumptions for selected parameters used to calculate dry deposition rates.
4. Passive monitoring of  $\text{SO}_2$  may be an acceptable approach for representing total S species dry deposition at remote locations within a region using the assumption of similar meteorological characteristics measured at dedicated monitoring sites. Estimates of annual S species deposition for the Alberta Environment Beaverlodge site during 1998 to 2002 indicated that consistently about 80% of S deposition was in the form of gaseous  $\text{SO}_2$  with the remainder as particulate sulphate.
  5. This was not the case for passive monitoring of  $\text{NO}_2$ . Passive monitoring does not appear to be an acceptable approach for representing total N species dry deposition at remote locations within a region using the assumption of similar meteorological characteristics measured at dedicated monitoring sites. Other N species deposition, e.g.  $\text{HNO}_3$ , may be as or more important. Estimates of annual N species deposition for the Alberta Environment Beaverlodge site during 1998 to 2002 indicated that ~35 to 50% of N deposition was from  $\text{NO}_x$  with the remainder as  $\text{HNO}_3$  and  $\text{HNO}_2$  (~40 to 60%) and particulate ammonium and nitrate (<10%). Estimates of annual N species deposition in the south western region of Alberta was reported as part of the Alberta Government/Industry Acid Deposition Research Program during 1985 to 1987. These estimates indicated that ~32% of N deposition was from  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) with the remainder as nitric and nitrous acid (~63%) and particulate nitrate (~5%). This is consistent with findings for the Alberta Environment Beaverlodge site during 1998 to 2002.
  6. Calculations undertaken to examine the effect of combining meteorological data and gaseous  $\text{SO}_2$  concentration data from Beaverlodge, Alberta as monthly time interval values tended to demonstrate similar deposition loadings. Annual 1998 and 1999  $\text{SO}_2$  deposition loadings based on computing monthly-average gaseous  $\text{SO}_2$  and meteorological values were within 8% of the current approach (deposition calculated as hourly average values and summed over a month). While both approaches are resource intensive, either are readily handled with today's computing software capabilities.



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## 1.0 INTRODUCTION

Acid deposition occurs when acidifying pollutants emitted from anthropogenic and other processes undergo complex chemical reactions in the atmosphere and fall to the earth as wet deposition (rain, snow, cloud, fog) or dry deposition (dry particles, gas). The main chemical precursors leading to acidic pollutants are sulphur dioxide ( $\text{SO}_2$ ) and oxides of nitrogen ( $\text{NO}_x$ ). Reactions of these pollutants with water, oxygen, carbon dioxide, and sunlight in the atmosphere produce acidic pollutants, e.g. sulphuric acid ( $\text{H}_2\text{SO}_4$ ) and nitric acid ( $\text{HNO}_3$ ). These and other acidic pollutants can be transported long distances in the atmosphere from their sources and eventually be deposited in ecosystems over broad regional scales and in locations far from the emission sources.

The process of dry deposition refers to removal of aerosol pollutants through eddy diffusion and impaction, large particles through gravitational settling, and gaseous pollutants through direct transfer from the air to the water via gas exchange. Dry deposition involves acidic sulphur and nitrogen pollutants (gases or particles) from the atmosphere being retained by the earth's surface. At the same time, co-deposition of base cations (e.g.  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$ ) results in a reduction of the amount of deposited acidity.

Potential acid input (PAI) provides a convenient method of representing the total acidic deposition. PAI includes both wet and dry deposition. PAI is calculated by subtracting the neutralizing capacity (base cation deposition) from the estimated deposition of acidic substances (e.g. sulphur plus nitrogen species). Cheng et al. (2001, 1997) provide a detailed description of the estimation of total PAI. The PAI method does not include processes that remove acidity from the earth's surface (leaching, runoff, etc.). It is an estimation of the total potential acid input into the system (AENV, 1999). A portion of the deposited potentially acidifying substances will not be available to contribute to acidification at the surface due to these removal processes.

Wet and dry deposition of each acidifying substance and base cations must be monitored in order to measure PAI (AENV, 1999). Monitoring of wet deposition of acidifying substances and base cations is simple, requiring the collection of precipitation (rain, snow) and laboratory analysis of the collected precipitation samples. Direct monitoring of dry deposition at the earth's surface is not possible at this time. At present, monitoring of ambient concentrations of acidifying substances in air is used. Estimation of dry deposition is then based upon these ambient measurements multiplied by a deposition velocity for each substance.

### 1.1 Objectives of Study

Currently there is no standard method for the field measurement and estimation of dry deposition of acidifying pollutants released into the environment. The objectives of this study were to examine current approaches used for measuring and estimating dry deposition and to identify whether a relatively economical technical approach can be put into practice for measuring and



estimating dry deposition of acidic substances across airsheds in Alberta. In an ideal case such an approach can lead to:

- Supporting the development of a more-comprehensive network of airshed monitoring for acidic substances.
- Expanded and enhanced provincial air quality monitoring of acidic substances.
- Further developing and implementing a better management approach for acid deposition in the province.



## 2.0 MEASURING AND ESTIMATING DRY DEPOSITION

Dry deposition is generally far more a local problem than wet deposition. Estimating dry deposition rates is more difficult. Dry deposition depends on many factors, including: meteorological conditions, characteristics of the pollutants being deposited (e.g. particle size), and characteristics of the surface on which deposition occurs (US EPA, 2001). A common approach to indirectly estimate dry deposition rates is on the basis of routinely measured air concentrations and meteorological parameters.

### 2.1 Routinely Measured Pollutants and Meteorological Parameters

Continuous and/or integrated measurement techniques are used to record the concentrations of atmospheric pollutants and continuous measurement techniques are used to record meteorological parameters. These parameters are needed to estimate dry deposition of atmospheric pollutants using the most common method – the inference method – described in the next section.

*Atmospheric Pollutants.* Atmospheric pollutants that are commonly measured for dry deposition using the inference method include:

- Sulphur compounds (gaseous  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$  in particulate matter).
- Nitrogen compounds (gaseous  $\text{NO}_2$ ,  $\text{HNO}_3$ , and  $\text{HNO}_2$ ; and  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in particulate matter).
- $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$  in particulate matter (co-deposition of these base cations results in a reduction of the amount of deposited acidity, thus these parameters are commonly measured).

Wesely and Hicks (2000) report that NO dry deposition is usually negligible because of its low solubility and low oxidizing capacity. It is usually not considered for measurement. Cheng et al. (2001) recommend that gaseous ammonia ( $\text{NH}_3$ ) not be considered when estimating dry deposition because sufficient understanding of its biochemistry has yet to be achieved.

Concentrations of the eleven substances measured above are combined into Equation 1 to estimate the potential acid input surface load in kilogram hydrogen equivalents (Cheng et al., 2001):

$$\text{PAI}_{\text{dry}} = \frac{[\text{SO}_2]}{64} + \frac{[\text{NO}_2]}{46} + \frac{[\text{HNO}_2]}{47} + \frac{[\text{HNO}_3]}{63} + 2\frac{[\text{SO}_4^{2-}]}{96} + \frac{[\text{NO}_3^-]}{62} + \frac{[\text{NH}_4^+]}{18} - \left( \frac{[\text{K}^+]}{39} + \frac{[\text{Na}^+]}{11} + 2\frac{[\text{Ca}^{2+}]}{40} + 2\frac{[\text{Mg}^{2+}]}{24} \right) \quad (1)$$

The units of each substance are in kg/ha/yr.



*Meteorological Parameters.* The continuous measurement of numerous meteorological parameters is necessary to allow estimation of dry deposition of the primary gaseous pollutants to specific surfaces using the inference method. Meteorological variables ultimately required are the 15-minute or one-hour standard deviation of wind direction, wind speed, solar radiation, and air temperature at standard height (10 m) and near the surface (2 m) (after EPCM, 2000). These temperatures are used to establish atmospheric stability. The presence or absence of a wet surface also affects dry deposition. Consequently, continuous measurement of the following meteorological parameters is required for estimating dry deposition using the inference method:

- Wind speed and wind speed standard deviation
- Wind direction and wind direction standard deviation
- Solar radiation
- Relative humidity
- Surface wetness
- Air temperature at standard height (10 m)
- Difference in air temperature at standard height and surface (taken as 2 m above ground).

## 2.2 Inference Method for Estimating Dry Deposition

The most accepted and common method for estimating dry deposition in North America, using measurement data described previously, is the so-called “inference method.” For example, forms of the inference method are used by Alberta Environment (Cheng et al., 2001), Environment Canada (Brook et al, 1999a), and the US Environmental Protection Agency (EPA) (Clarke et al., 1997).

The inferential method involves indirect estimation of dry deposition rates on the basis of routinely measured air concentrations and meteorological parameters. The method is based on an assumed steady-state relationship  $F = V_d C$ , where the dry deposition flux or rate ( $F$ ) is a product of the dry deposition velocity ( $V_d$ ) and the concentration ( $C$ ) of an airborne pollutant.  $V_d$  is estimated on the basis of resistance models and can be defined as the inverse of the sum of multiple resistance factors (aerodynamic resistance ( $R_a$ ), boundary-layer resistance ( $R_b$ ), and surface resistance ( $R_c$ )) (Wesely and Hicks, 2000, 1977):

$$V_d = (R_a + R_b + R_c)^{-1} \quad (2)$$

Figure 1 illustrates the relative locations where dry deposition resistance factors  $R_a$ ,  $R_b$ , and  $R_c$  apply near a surface.

*Aerodynamic Resistance ( $R_a$ ).* A shallow sublayer occurs next to the ground that is within the atmospheric constant flux layer. The depth of this layer is in terms of meters (m) and depends upon atmospheric turbulence and stability, and surface characteristics (Cheng et al., 2001). The atmospheric resistance term,  $R_a$ , is used to parameterize the rate of pollutant transfer within this sublayer as a function of atmospheric turbulence and stability, and surface characteristics (Wesely and Hicks, 1977).





**Figure 1. Relative locations where dry deposition resistance factors  $R_a$ ,  $R_b$ , and  $R_c$  apply.**

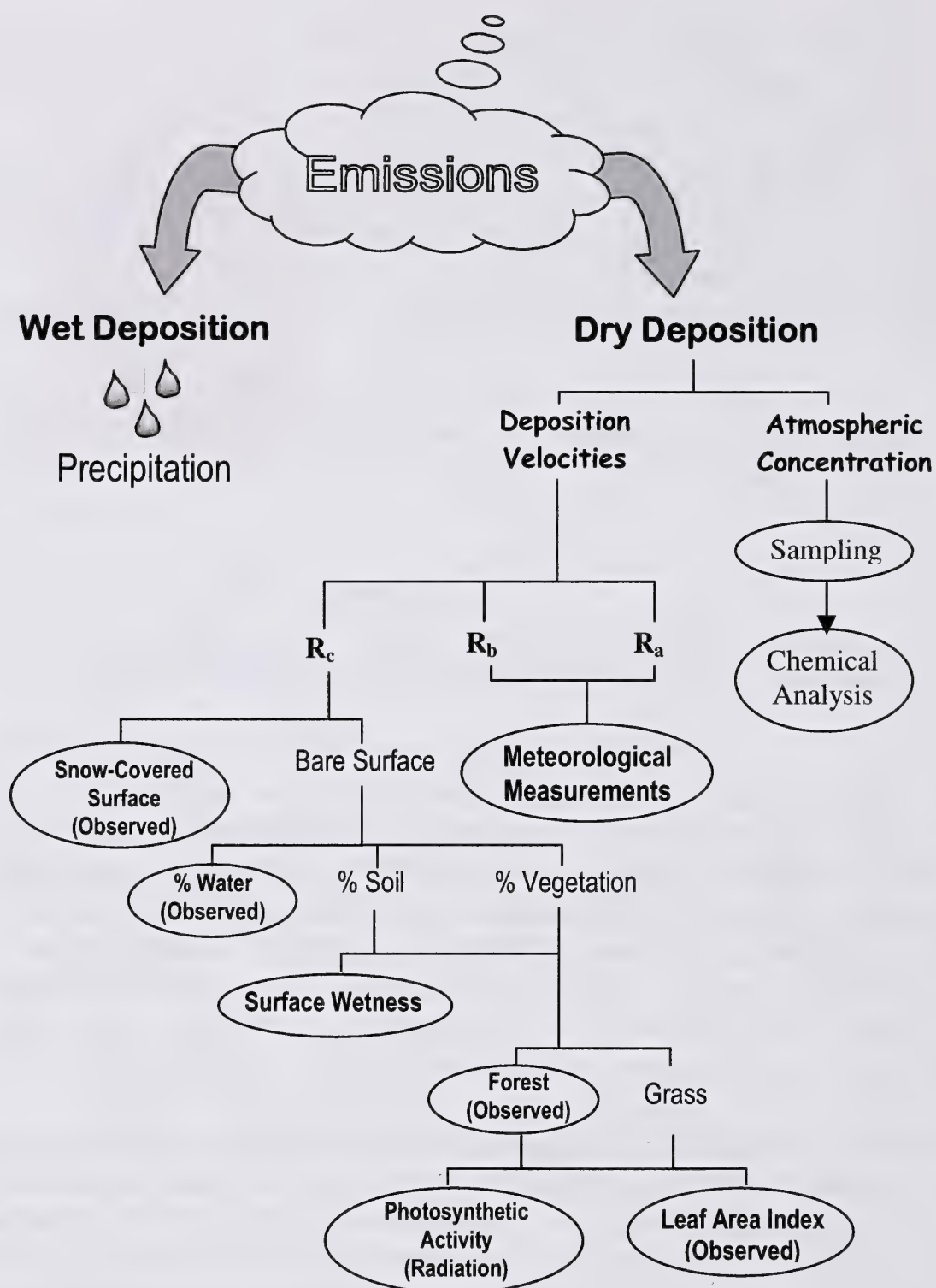
*Boundary-layer Resistance ( $R_b$ ).* The boundary layer is a thin, non-turbulent layer that develops just above the surface. The depth of this layer is in terms of millimeters (mm). For rough surfaces, this layer is constantly changing and Hicks (1982) reported that it is likely to be intermittently turbulent. The rate of pollutant transfer within this layer is determined by molecular diffusion for gases and Brownian diffusion and inertial impaction for particles. The boundary-layer resistance term,  $R_b$ , is usually parameterized in terms of the Schmidt number (viscosity of air divided by the diffusivity of the pollutant) and, for particles, the Stokes number (which is a function of the gravitation settling velocity, friction velocity, and the viscosity of air).

*Surface Resistance ( $R_c$ ).* Vegetation is a major sink for many soluble or reactive gaseous pollutants. After passing through the stomata of vegetation, soluble pollutants dissolve in the moist mesophyll cells in the interior of the leaves (Wesely and Hicks, 1977). Reactive pollutants, e.g. ozone, may also interact with the exterior (cuticle) of the leaves. Due to the response of the stomata to external factors such as moisture stress, temperature, and solar radiation, resistance in the vegetation layer can exhibit significant diurnal and seasonal variability. The surface resistance term,  $R_c$ , is usually parameterized in terms of the three main pathways for uptake/reaction of the pollutant within the vegetation or surface (Wesely and Hicks, 1977):

- Transfer through the stomatal pore and dissolution or reaction in the mesophyll cells.
- Reaction with or transfer through the leaf cuticle.
- Transfer into the ground/water surface.

Figure 2 further illustrates components that are measured and/or observed in estimating the surface resistance factor (after Cheng et al., 2001).





**Figure 2. Components measured and/or observed in estimating the surface resistance factor,  $R_c$  (after Cheng et al., 2001).**

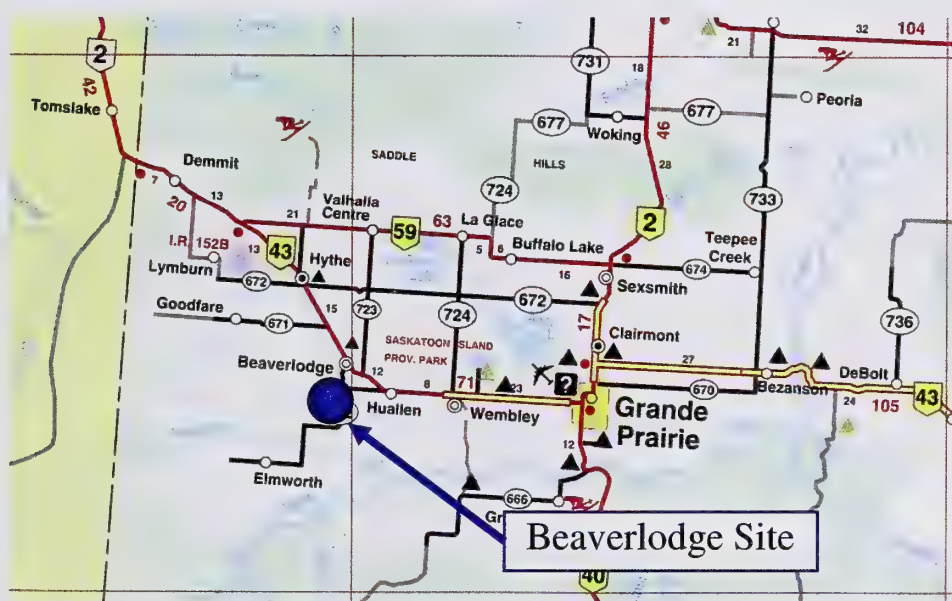


## 2.3 Review of Methods

Monitoring of dry deposition of acidic parameters is carried out in Alberta by a number of organizations. Historically, Alberta Environment has monitored acidic parameters in Royal Park (Bates, 1996) and Beaverlodge (Aklilu, 1999). Dry deposition monitoring is also carried out in the West Central Airshed Society zone and Wood Buffalo Environmental Association zone. Monitoring of dry deposition of acidic parameters is carried out by Environment Canada (Brook et al, 1999a) and the US Environmental Protection Agency (EPA) (Clarke et al., 1997).

### 2.3.1 Alberta Environment

Dry deposition and meteorological parameters were monitored by Alberta Environment at Beaverlodge, Alberta up to the end of 2002 using the URG integrated VAPST<sup>TM</sup> (Versatile Air Pollutant Sampling) system. The Beaverlodge station is located west of Grande Prairie at the Agriculture and Agri-food Canada Research Farm (Figure 3).



**Figure 3** Location of former Alberta Environment dedicated “acid deposition” monitoring site near Beaverlodge, Alberta (not to scale).

The Beaverlodge station measured the following parameters needed to reconstruct estimates of dry deposition loads:

1. Acidic parameters:

- Atmospheric gases –
  - continuous NO<sub>x</sub>
  - one 24-hour integrated VAPST<sup>TM</sup> sample for SO<sub>2</sub>, HNO<sub>2</sub>, HNO<sub>3</sub>, and NH<sub>3</sub> every 6<sup>th</sup> (or 12<sup>th</sup>) day
- Particulate matter (PM<sub>10</sub>) – one 24-hour integrated sample every 6<sup>th</sup> (or 12<sup>th</sup>) day –
  - Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup>



## 2. Meteorological parameters:

- Wind speed and wind speed standard deviation
- Wind direction and wind direction standard deviation
- Solar radiation
- Relative humidity
- Surface wetness
- Dew point temperature
- Air temperature at standard height (10 m)
- Difference in air temperature at standard height and surface (taken as 2 m above ground)

The sampling program was based on collecting data on acidic and meteorological parameters in order to estimate dry deposition using a form of the inferential method. The specific relationships used to estimate aerodynamic ( $R_a$ ), boundary-layer ( $R_b$ ), and surface (canopy) resistances ( $R_c$ ) by Alberta Environment are described in Appendix I (after Cheng et al., 2001). Surface resistance ( $R_c$ ) is calculated based on surface type, surface wetness, and incident radiation characteristics. The influence of meteorological conditions, vegetation, and chemistry in estimating deposition is simulated by the deposition velocity ( $V_d$ ) in Equation 2.

Hourly deposition fluxes for each species are calculated as the product of the hourly  $V_d$  obtained and the corresponding hourly concentration. Hourly concentrations are obtained from 24-hour VAPs and  $PM_{10}$  sample results and measured hourly  $NO_x$  concentrations. All hourly concentrations during a VAPs and  $PM_{10}$  sampling run were assumed to be equal to the sample concentration and constant for a duration between the sampling periods. That is to say, if a VAPs or  $PM_{10}$  sample were obtained every 12<sup>th</sup> day, the hourly concentration of a species was assumed to be equal to the VAPs or  $PM_{10}$  sample result for 12 days x 24 hr/day, or 288 consecutive hourly periods.

### 2.3.2 *Airsheds in Alberta*

#### **West Central Airshed Society**

The West Central Airshed Society (WCAS) and power plant operators (EPCOR and TransAlta) are developing an acid deposition passive monitoring program in response to operation of four coal-fired power plants west of Edmonton, Alberta (Scotten, 2004). This program consists of two dedicated “acid deposition” monitoring sites and a rural passive monitoring network.

*Dedicated Acid Deposition Monitoring Sites* – WCAS operates two stations – Genesee and Violet Grove – that serve as “dedicated” acid deposition monitoring sites. The location of these two stations is shown in Figure 4.

The Genesee station currently measures the following parameters needed to reconstruct estimates of dry deposition loads:

1. Acidic parameters:
  - Atmospheric gases –
    - continuous  $SO_2$  and  $NO_2$

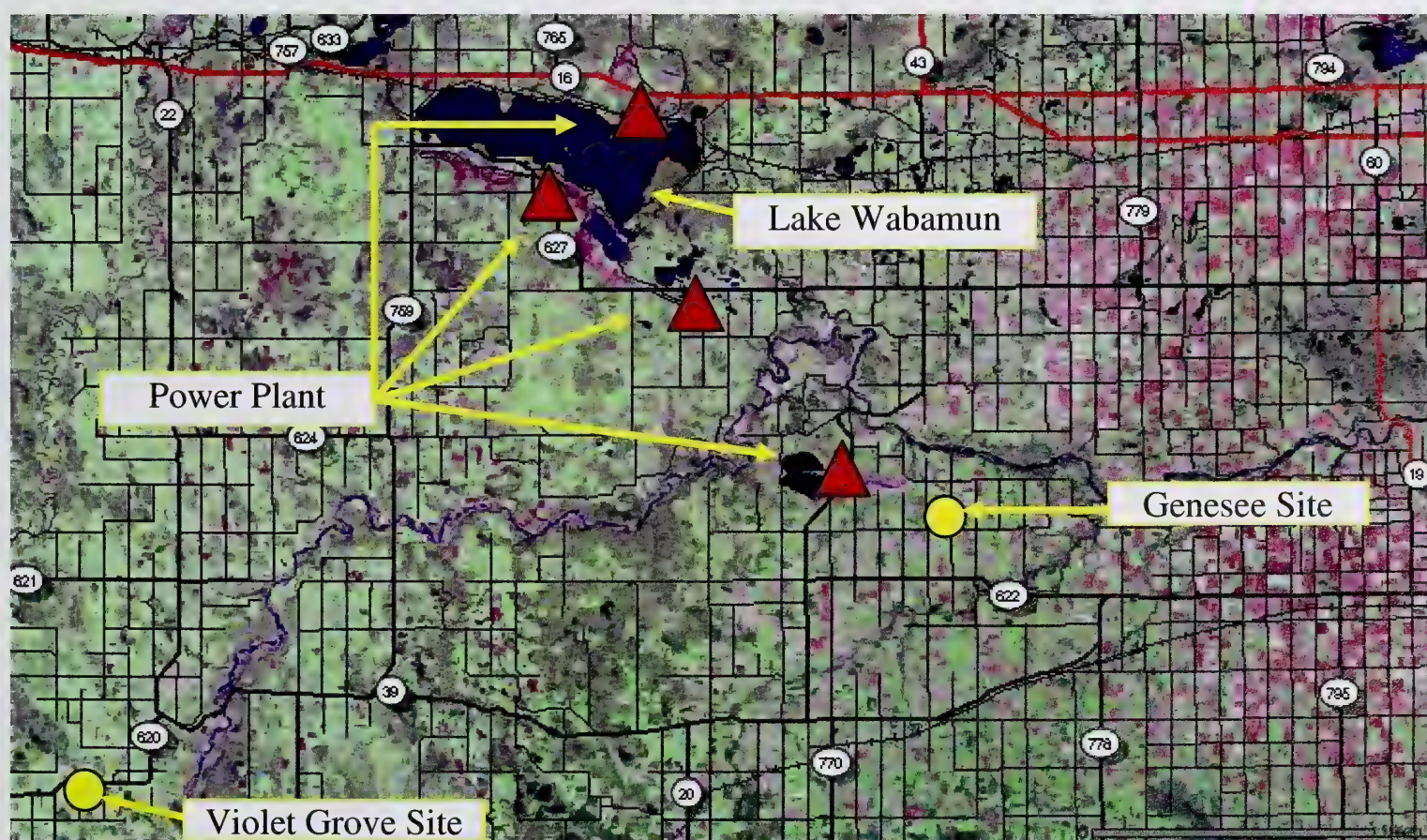


- monthly integrated passive sample of  $\text{SO}_2$  and  $\text{NO}_2$
- monthly integrated annular denuder sample for  $\text{HNO}_2$ ,  $\text{HNO}_3$ , and  $\text{NH}_3$
- Particulate matter (TSP) – one 24-hour integrated sample every 6<sup>th</sup> day –
  - $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$
- Chemistry from precipitation samples integrated monthly (wet deposition component) –
  - pH,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$

2. Meteorological parameters:

- Precipitation amounts
- Wind speed and wind speed standard deviation
- Wind direction and wind direction standard deviation
- Solar radiation
- Relative humidity
- Surface wetness
- Air temperature at standard height (10 m)
- Difference in air temperature at standard height and surface (taken as 2 m above ground)

The Genesee air monitoring station only became fully operational in December 2004.



**Figure 4** Location of dedicated “acid deposition” monitoring sites in West Central Airshed Society zone (not to scale).

In addition to the Genesee air monitoring station, WCAS operates another monitoring site outside of the air monitoring area for power plants – the Violet Grove station. This station is located in an area where expected acid loading conditions are lower than that for the Genesee



station location. This arrangement (Genesee and Violet Grove) is intended to acquire data on acid loading variation within the eastern area of the WCAS zone where the four coal-fired power plants operate.

The Violet Grove station currently measures the following parameters (similar to Genesee):

1. Acidic parameters:

- Atmospheric gases –
  - continuous SO<sub>2</sub> and NO<sub>2</sub>
  - monthly integrated annular denuder sample for HNO<sub>2</sub>, HNO<sub>3</sub>, and NH<sub>3</sub>
- Particulate matter (TSP) – 24-hour integrated sample every 6<sup>th</sup> day –
  - Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup>
- Chemistry from precipitation samples integrated monthly (wet deposition component) –
  - pH, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>

2. Meteorological parameters:

- Precipitation amounts
- Wind speed and wind speed standard deviation
- Wind direction and wind direction standard deviation
- Solar radiation
- Relative humidity
- Surface wetness
- Air temperature at standard height (10 m)
- Difference in air temperature at standard height and surface (taken as 2 m above ground)

*Rural Passive Monitoring Network* – A rural passive monitoring program is being developed by WCAS and power plant operators (EPCOR and TransAlta) (Scotten, 2004). The program will have 10 rural sites where monthly SO<sub>2</sub> and NO<sub>2</sub> measurements are taken. This will include nine sites in an approximate 3 by 3 grid arrangement in the air monitoring area for power plants and one site to the west of the air monitoring area. These rural sites are intended to become operational in fall 2005 and to operate for a 3- to 5-year period.

The WCAS program is based on collecting data on acidic and meteorological parameters in order to estimate dry deposition using a form of the inferential method. Meteorological measurements and similar relationships used by Alberta Environment (described in Appendix I) are used to estimate aerodynamic (R<sub>a</sub>) and boundary-layer (R<sub>b</sub>) resistances. Historical (pre-2000) methods for estimating surface (canopy) resistance (R<sub>c</sub>) were similar to relationships used by Alberta Environment described in Appendix I. All hourly concentrations during an annular denuder sampling period are assumed to be equal to the sample concentration and constant for the duration of the sample. Methods employed since 2000 have only addressed estimating dry deposition of gaseous parameters (SO<sub>2</sub> and NO<sub>2</sub>/NO). However, the intent is to take into account all acidic parameters in future dry deposition calculations (Scotten, 2004).

## **Wood Buffalo Environmental Association**

The Wood Buffalo Environmental Association currently operates one dedicated “acid deposition” monitoring station and the Terrestrial Environmental Effects Program (TEEM)



passive SO<sub>2</sub>/NO<sub>2</sub> monitoring program in the oil sands area north of Fort McMurray. This is described further below.

*Dedicated Acid Deposition Monitoring Site* – A monitoring station located outside of Fort McKay, Alberta serves as a dedicated acid deposition site (WBEA Air Monitoring Station #1). With respect to acid deposition, this station measures the following parameters:

1. Acidic parameters:

- Atmospheric gases –
  - continuous SO<sub>2</sub> and NO<sub>2</sub>
  - monthly integrated passive sample of SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub>
  - 24-hour integrated annular denuder sample every 6<sup>th</sup> day for HNO<sub>2</sub>, HNO<sub>3</sub>, and NH<sub>3</sub>
- Particulate matter (PM<sub>2.5</sub> and PM<sub>10</sub>) – 24-hour integrated sample every 6<sup>th</sup> day –
  - Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup>
- Chemistry from precipitation samples integrated intermittently after occurrence of precipitation events (wet deposition component) –
  - pH, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, total alkalinity

2. Meteorological parameters:

- Precipitation amounts
- Wind speed and wind speed standard deviation
- Wind direction and wind direction standard deviation
- Solar radiation
- Relative humidity
- Surface wetness
- Air temperature at standard height (10 m)
- Difference in air temperature at standard height and surface (taken as 2 m above ground).

*Rural Passive Monitoring Network* – The WBEA TEEM Program operates ten passive monitoring sites to measure concentrations of SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub> at remote forest locations. These ten sites along with the Fort McKay stations are shown in Figure 5. In addition, four passive monitoring sites are located around the Petro-Canada MacKay River Project. These sites monitor concentrations of SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub>, and H<sub>2</sub>S.

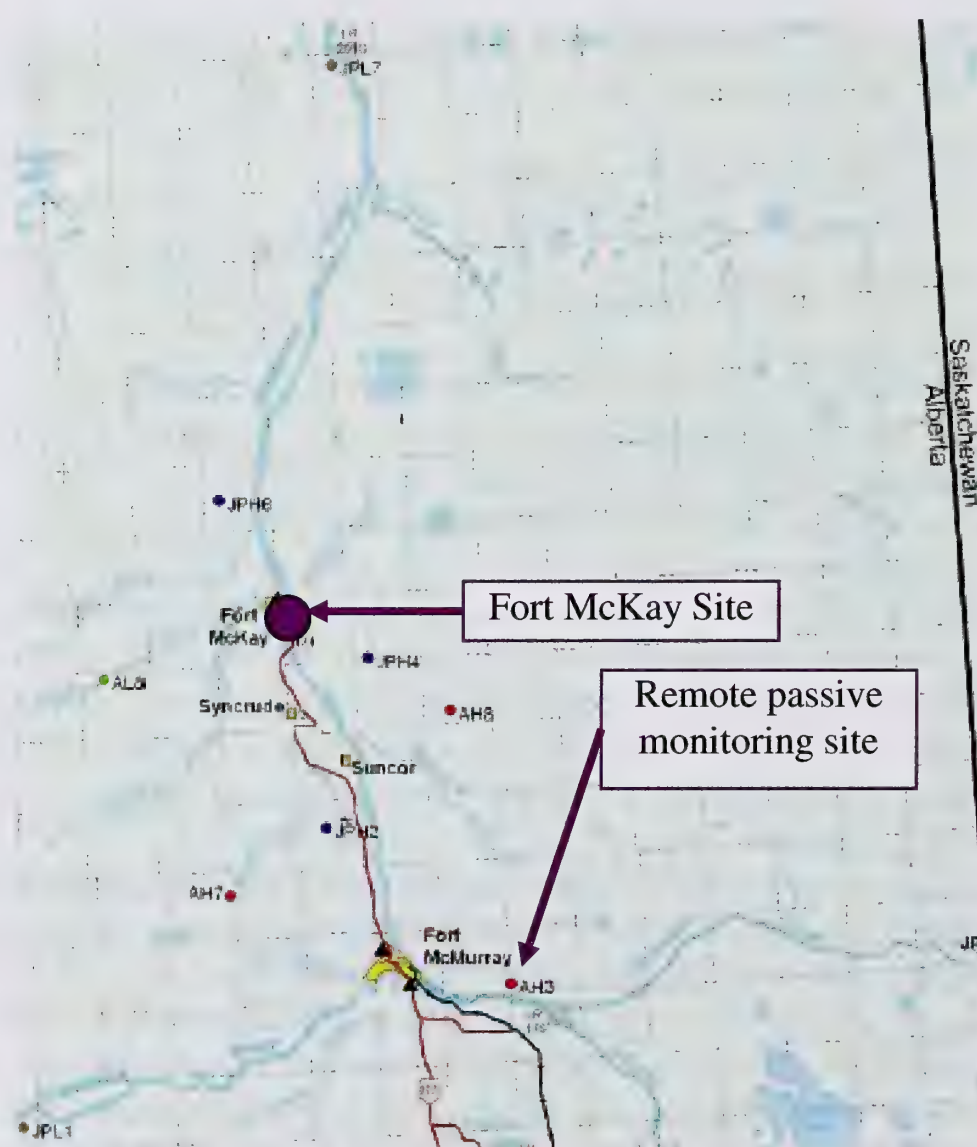
The program is based on collecting data on acidic and meteorological parameters in order to estimate dry deposition using a form of the inferential method. Meteorological measurements and similar relationships used by Alberta Environment (described in Appendix I) are used to estimate aerodynamic (R<sub>a</sub>) and boundary-layer (R<sub>b</sub>) resistances. Surface (canopy) resistance (R<sub>c</sub>) is estimated using a Leaf Area Index (LAI) method similar to relationships described in the CALPUFF dispersion model after Scire et al. (2000) and using default assumptions presented in EPCM (2002). These relationships are described further in Appendix II.



### 2.3.3 *Environment Canada*

A national dry deposition monitoring network is operated in Canada by Environment Canada. It is Environment Canada's Canadian Air and Precipitation Monitoring Network (CAPMoN, [http://www.msc-smc.ec.gc.ca/capmon/index\\_e.cfm](http://www.msc-smc.ec.gc.ca/capmon/index_e.cfm)). CAPMoN is operated by the Meteorological Service of Canada (MSC) in order to study regional patterns and trends of acid rain, air and precipitation chemistry.

CAPMoN measures wet deposition (through rain or snow) and (inferential) dry deposition, as well as the ambient concentrations of acid forming gases and particles. The network began operating in mid-1983 when it updated and replaced two older networks known as the Canadian Network for Sampling Precipitation (CANSAP) and the Air and Precipitation Network (APN). Integration of APN as part of CAPMoN extended the data records as far back as 1978 (MSC, 2005a).



**Figure 5** Location of dedicated “acid deposition” monitoring site (Fort McKay) and ten remote passive monitoring sites in Wood Buffalo Environmental Association zone (after EPCM, 2002).



Objectives of CAPMoN are to (MSC, 2005a):

- Determine spatial patterns and establish temporal trends of atmospheric pollutants related to acid rain and smog.
- Provide data for long-range transport model evaluations and effects research (aquatic and terrestrial).
- Ensure compatibility of Federal, Provincial and U.S. measurements.
- Study atmospheric processes.

There have been as many as 43 CAPMoN sites over the years, but no more than 26 have operated simultaneously. Presently, there are 18 sites as part of the network (MSC, 2005a). CAPMoN sites were originally chosen in non-urban areas to avoid local pollution sources and to minimize local influences on precipitation quality and quantity. Precipitation is collected as a 24-hour integrated sample at all CAPMoN sites. Parameters measured include: pH, sulphate, nitrate, chloride, ammonium, sodium, calcium, magnesium, and potassium.

CAPMoN also collects integrated particle and trace atmospheric gas samples at a subset of 10 sites, although as many as 16 sites were once engaged in this activity (MSC, 2005a). The current air monitoring sites are located in:

- Ontario (Longwoods, Experimental Lakes Area, Algoma, Chalk River, and Egbert)
- Quebec (Chapais and Sutton)
- Nova Scotia (Kejimikujik)
- British Columbia (Saturna)
- Saskatchewan (Brad Lake)

There is also a special site located at the Pennsylvania State University in United States for comparison between CAPMoN and the US National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Parameters measured include: particulate sulphate, nitrate, chloride, ammonium, sodium, calcium, magnesium, and potassium, as well as vapor phase  $\text{HNO}_3$  and  $\text{SO}_2$ . Hourly average tropospheric (ground-level) ozone measurements are made at six sites.

Particle and trace gas concentrations are determined using 24-hour integrated filter measurements (Zhang et al., 2001). The filters are designed to measure specific gases and particles in air that contribute to dry deposition. CAPMoN uses 47 mm filter media contained in an open-faced three stage filter pack mounted at a height of 10 metres. The filter pack contains a Teflon filter for collection of particulate species, a nylon filter for  $\text{HNO}_3$  and a base-impregnated cellulose (Whatman) filter for  $\text{SO}_2$ .

A control unit sequences the flow through a different filter pack every 24 hours at 08:00 LST. The air flow through the filter pack is maintained at 25 lpm by a mass flow controller (Zhang et al., 2001). All filters are shipped to the CAPMoN laboratory in Ottawa for chemical analysis. Although they are required for calculations of dry deposition rates, it is not clear what meteorological measurements are made at the CAPMoN sites, nor if information on land use and vegetation is collected.



In general, the network design is based on inferential methods, which work on the assumption that dry deposition or flux can be estimated as the linear product of ambient concentration (C) and deposition velocity ( $V_d$ ) (Wesely and Hicks, 2000; Wesely, 1989). The influence of meteorological conditions, vegetation, and chemistry is simulated by  $V_d$ . It appears Environment Canada and others have utilized numerous different models to attempt to calculate dry deposition values for data collected through CAPMoN. For example, inferential approaches coupled with modeling that extends site-specific estimates to wider areas have been applied in CAPMoN (Sirois and Barrie, 1988). Big Leaf models and land-use based models have also been used in the past to estimate the relative importance of dry versus wet deposition over selected Canadian regions (Brook et al., 1996).

Environment Canada has developed a detailed dry deposition model for routine computation of dry deposition velocities – referred to as the Routine Deposition Model (RDM) (Brook et al., 1999a). Four different dry deposition/surface exchange sub-models were combined with the current Canadian weather forecast model (Global Environmental Multiscale model) with a 3-hour time resolution and a horizontal spatial resolution of 35 km. The RDM uses US Geological Survey North American Land Cover Characteristics data to obtain fourteen different land use and five seasonal categories.

The four sub-models used are (Brook et al., 1999a):

- A multi-layer model for gaseous species over taller canopy land-use types.
- A Big Leaf model for gaseous species over lower canopies (including bare soil and water) and for  $\text{HNO}_3$  under all surface types.
- Two different models for  $\text{SO}_4^{2-}$  - one for tall canopies and the other for short canopies.

The purpose for developing this detailed model with the four sub-models was to provide estimates of seasonal dry deposition, which can be combined with wet deposition to produce total deposition estimates. Based on results of extensive model runs, it was demonstrated that the RDM  $V_d$  values can be combined with measured air concentrations over hourly, daily, or weekly periods to determine dry deposition amounts and with wet deposition measurements to provide seasonal estimates of total deposition and estimates of the relative importance of dry deposition (Brook et al., 1999b).

The more recent approach to provide deposition estimates by Environment Canada is known as A Unified Regional Air Quality Modeling System (AURAMS) (Zhang et al., 2002a; MSC, 2005b). AURAMS is intended to provide a better understanding of particulate matter and other regional pollutants in North America, and especially in Canada. The model is capable of assessing the impact of emission reduction scenarios separately or simultaneously for particulate matter, ground-level ozone, acidic deposition, and eventually air toxics (Zhang et al., 2002a).

Dry deposition is an important process that requires treatment in AURAMS. A size-segregated particle dry deposition module originally developed by MSC (Zhang et al., 2001) is incorporated into AURAMS to treat particle dry deposition. For gaseous deposition, a Big Leaf model is used for AURAMS. The reason for this choice of model was the need to balance accuracy, complexity, and computational cost of parameterization for dry deposition with parameterizations of the many other processes represented (Zhang et al., 2002a). Another reason



for choosing the dry-deposition scheme was that such schemes were judged to be likely to produce deposition estimates that are reliable to or representative of results from more sophisticated schemes.

Existing Big Leaf models could not be adopted directly, however, due to the fact that the AURAMS gas-phase chemical mechanism has many additional chemical species for which dry deposition must also be addressed (Zhang et al., 2002a). Besides the gaseous species that are usually considered by the dry-deposition community there are more than 40 other AURAMS species that are long-lived enough for transport to be considered and whose dry deposition may also need to be represented. The land-use categorization used by AURAMS is also different and thus some adaptation was required. Therefore, a new Big Leaf model was designed by Environment Canada to deal with these issues (Zhang et al., 2002a).

Although the models were judged to perform well, AURAMS was recently revised to incorporate an improved dry deposition parameterization scheme for air quality models by including non-stomatal resistance parameterizations (Zhang et al., 2003b). The Big Leaf model developed by Zhang et al. (2002a) was developed for calculating dry deposition velocities for more than 40 gaseous species for AURAMS, but it only included seasonally-adjusted values for non-stomatal resistance. The revised model incorporates these non-stomatal resistance parameterizations (Zhang et al., 2003a; Zhang et al., 2002b). Other improvements to the previous model include more realistic treatment of cuticle and ground resistance in winter and the handling of seasonally-dependent input parameters.

### **2.3.4 US Environmental Protection Agency**

In 1986 the US Environmental Protection Agency (EPA) established the National Dry Deposition Network (NDDN) to obtain field data on rural deposition patterns and trends at different locations throughout the United States (Clarke et al., 1997). At the time, the network consisted of 50 monitoring sites that derived dry deposition based on measured air pollutant concentrations and modeled dry deposition velocities estimated from meteorology, land use, and site characteristic data. In 1990, amendments to the Clean Air Act brought about the implementation of a long-term, national program to monitor the status and trends of air pollutant emissions, ambient air quality, pollutant deposition, and ecological effects. In response, the US EPA developed the Clean Air Status and Trends Network (CASTNet, [www.epa.gov/CASTNet/](http://www.epa.gov/CASTNet/)).

CASTNet provides atmospheric data on dry deposition components of total acid deposition, ground-level ozone, and other forms of atmospheric pollution (Clarke et al., 1997). CASTNet is considered the nation's primary source for atmospheric data to estimate dry acidic deposition and to provide data on rural ozone levels. The primary objectives of CASTNet are to (US EPA, 2005):

- Monitor the status and trends in regional air quality and atmospheric deposition.
- Provide information on the dry deposition component of total acid deposition, ground level ozone, and other forms of atmospheric gaseous and aerosol pollution.
- Assess and report on geographic patterns and long-term, temporal trends in ambient air pollution and acid deposition.



Currently CASTNet is comprised of approximately 86 monitoring stations across the United States and one in Canada (Figure 6) (US EPA, 2005). The US EPA Office of Air and Radiation operates the majority of the monitoring stations; however, the US NPS operates approximately 30 stations in cooperation with US EPA. In addition, wet deposition is monitored at approximately 240 National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites, with an NADP/NTN site either collocated or located within 50 km of each CASTNet site (Clarke et al., 1997).

Together, long-term data collect by these two networks provide the necessary data to estimate trends and spatial patterns in total atmospheric deposition (Clarke et al., 1997). Monitoring site locations are predominantly rural by design to assess the relationship between regional pollution and changes in regional patterns in deposition. Rural monitoring sites provide data where sensitive ecosystems are located and provide insight into natural background levels of pollutants where urban influences are minimal.



**Figure 6. Current CASTNet dry deposition monitoring sites in United States (after US EPA, 2005).**



Each of CASTNet's approximately 87 dry deposition stations measures the following parameters on a 7-day (168 hours, Tuesday to Tuesday) schedule (MACTEC, 2003a):

1. Ambient measurements:

- Gaseous: sulphur dioxide ( $\text{SO}_2$ ), nitric acid ( $\text{HNO}_3$ ), ozone ( $\text{O}_3$ )
- Particulate: sulphate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), calcium ( $\text{Ca}^{2+}$ ), sodium ( $\text{Na}^+$ ), magnesium ( $\text{Mg}^{2+}$ ), potassium ( $\text{K}^+$ )

2. Meteorological measurements (as hourly averages):

- Temperature at 9 meters
- Delta temperature between 2 and 9 meters
- Solar radiation
- Relative humidity
- Precipitation
- Scalar wind speed
- Vector wind speed
- Wind direction
- Standard deviation of wind speed within the hour (sigma theta)
- Rate of flow through the filter pack
- Surface wetness

3. Information on land use and vegetation:

- Site surveys
- Site operator observations (vegetation type, percent green leaf out)
- Leaf Area Index (LAI)

4. Trends:

- Concentrations of sulphur and nitrogen species and cations
- Deposition of sulphur and nitrogen
- Ozone concentrations

Meteorological variables and ozone concentrations are recorded continuously and reported as hourly averages (Clarke et al., 1997). Atmospheric sampling for sulphur and nitrogen species is integrated over weekly collection periods using an open-face, three-stage filter pack. The filter pack contains a Teflon filter for collection of particulate species, a nylon filter for nitric acid and a base-impregnated cellulose (Whatman) filter for sulphur dioxide. Filter packs are exposed for 1-week intervals at a flow rate of 1.5 lpm (3.0 lpm for western sites) and sent to the laboratory for chemical analysis.

Atmospheric concentrations are calculated based on the mass of analyte in each filter and volume of air sampled (MACTEC, 2003b):

- Atmospheric concentrations of particulates ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$ ) are calculated based on the analysis of Teflon filter extracts.
- $\text{HNO}_3$  is calculated based on  $\text{NO}_3^-$  found in nylon filter extracts.
- $\text{SO}_2$  is calculated based on the sum of  $\text{SO}_4^{2-}$  found in nylon and cellulose filter extracts.

In addition to the above, various observations are periodically made at CASTNet sites to support model calculations of dry deposition (Baumgardner Jr. et al., 2002). Site operators record surface conditions (e.g. dew, frost, snow) and vegetation status weekly. Vegetation data are



obtained to track evolution of the dominant plant canopy, from leaf emergence (germination) to senescence (harvesting). Once a year site operators provide information on major plant species and land-use classifications within 1 km of CASTNet sites. Additional land-use data are obtained by digitization and analysis of aerial photographs obtained from the US Geological Survey (USGS). Leaf area index (LAI) measurements have been conducted at all CASTNet sites using an LAI-2000 Plant Canopy Analyzer manufactured by Li-Cor (Lincoln, NE) (MACTEC, 2004).

The network design is based on the assumption that dry deposition or flux can be estimated as the linear product of ambient concentration ( $C$ ) and deposition velocity ( $V_d$ ) (Wesely and Hicks, 2000; Wesely, 1989).  $V_d$  simulates the influence of meteorological conditions, vegetation, and chemistry. Dry deposition processes are modeled as resistances to deposition (Myers et al., 1998). These resistances include aerodynamic resistance ( $R_a$ ), boundary layer resistance to vertical transport ( $R_b$ ), and surface uptake (canopy) resistance ( $R_c$ ).

Using this physical and mathematical framework, two dry deposition models – Big Leaf Model and the Multi-layer Model (MLM) – have been used to calculate dry deposition for CASTNet (Clarke et al., 1997). The Big Leaf model treats the vegetation canopy as a one-dimensional surface (Meyers et al., 1998). The MLM is a variation of the Big Leaf model wherein similar calculations are applied through a 20-layer canopy in which model parameters are modified by redistribution of heat, momentum, and pollutants (Meyers et al., 1998). The MLM requires hourly data on the following input parameters (Meyers et al., 1998): wind speed, wind direction, sigma theta, temperature, relative humidity, solar radiation, surface wetness, LAI, vegetative species, and percent green leaf out. The MLM also accounts for water and temperature stress as well as stomatal resistances of vegetation and deposition to snow surfaces.

Additionally, several parameters have been modified in the MLM from those used in the Big Leaf model (Sickles and Shadwick, 2002). The MLM model simulates variable soil moisture. The algorithm for soil uptake resistance was changed to account for presence of snow or for presence of certain crops and grasses. The minimum wind speed was changed from 0.2 to 0.1 m/sec and, if relative humidity is above 89%, surface wetness is set to 1.0.

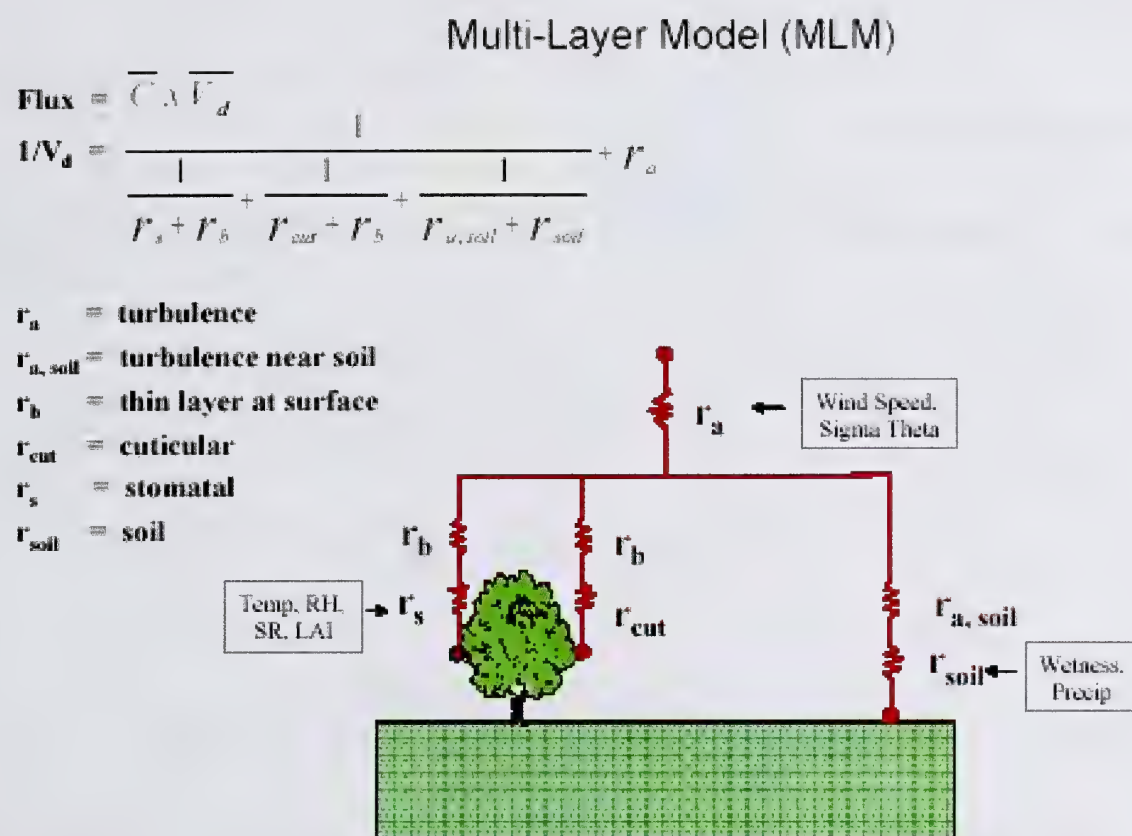
Dry deposition calculations to estimate  $V_d$  for each monitored chemical species at CASTNet sites are currently made using a version of the MLM updated in 1998 (Meyers et al., 1998). A schematic of the MLM is shown in Figure 7 depicting the relationships among various resistances and meteorological and other data that are required as inputs (MACTEC, 2003a).

Hourly deposition fluxes for each species are calculated as the product of the hourly  $V_d$  obtained from the MLM and the corresponding hourly concentration (MACTEC, 2003a). Hourly concentrations are obtained from weekly filter pack results and measured hourly ozone concentrations. All hourly concentrations during a filter pack sampling period are assumed to be equal to the filter pack sample concentration and constant for the duration of the sample.

Weekly deposition fluxes are the sum of valid hourly fluxes for a standard deposition week, divided by the ratio of valid hourly fluxes to the total number of hours in the standard week to account for missing or invalid values (MACTEC, 2003a). A standard deposition week is defined



as the 168-hour period from 0900 Tuesday to 0900 the following Tuesday. Similarly, quarterly fluxes are calculated from weekly values and annual values are calculated from quarterly values.



**Figure 7. Schematic of the Multi-Layer Model (after MACTEC, 2003a).**



## 3.0 DRY DEPOSITION MONITORING AND ESTIMATION APPROACH

### 3.1 General Approach

Given the types of field measurement methods currently being used to monitor and estimate dry deposition, a consistent regional approach is recommended to enable data to be used for interpretation at a provincial level. Current field measurement methods used as part of the regional approach were discussed previously in Section 2 and they involve:

- Integrated measurement techniques, e.g. Annular Denuder System or Versatile Air Pollution System monitoring of acidic gases ( $\text{HNO}_3$ ,  $\text{HNO}_2$ , and  $\text{NH}_3$  if desired) at “dedicated” acid deposition sites.
- Continuous measurement of atmospheric gases ( $\text{SO}_2$ ,  $\text{NO}_2$ ) at “dedicated” acid deposition sites.
- Integrated measurement techniques for ions in particulate matter ( $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{K}^+$ ) at “dedicated” acid deposition sites.
- Continuous measurement of meteorological parameters at “dedicated” acid deposition sites.
- Integrated (passive) measurement of atmospheric gases ( $\text{SO}_2$ ,  $\text{NO}_2$ ) at remote sites.

This general approach is described further in the following points:

1. At a larger – provincial – level, the *first important aspect* to consider in developing a network for dry deposition monitoring is that consistent (or comparable) sets of air pollutant and meteorological data need to be gathered at multiple sites within the province. If comparable monitoring approaches are employed among airsheds, data obtained can be used for interpretation at a provincial level.

Such an interpretation has relevance because Alberta Environment has adopted critical, target, and monitoring loadings for acid deposition in the province (AENV, 1999). The loadings are applicable to grid cells measuring  $1^\circ$  latitude x  $1^\circ$  longitude (approximately 110 x 60 km) across the province, with each cell being categorized as sensitive, moderately sensitive, or of low sensitivity on the basis of the sensitivities of the soil and water systems within the cell. Critical loads are set at 0.25, 0.50 and 1.00 keq  $\text{H}^+$   $\text{ha}^{-1}$   $\text{yr}^{-1}$  potential acid input (PAI) for grid cells categorized as sensitive, moderately sensitive, and of low sensitivity, respectively.

2. At a smaller – regional airshed – level, a *second important aspect* to consider in developing a network for dry deposition monitoring is that dry deposition is generally far more important locally than wet deposition (i.e. near important sources) (US EPA, 2001). This indicates that at least one “dedicated” acid deposition monitoring site should be located near important source emitting areas to take necessary air pollutant and meteorological measurements for estimating dry deposition.



3. A *third important aspect* for airshed network monitoring is having an ability to detect variation within a monitored area. This is particularly important when using monitoring techniques for which no standard methods exist, such as dry deposition monitoring. In this situation it would be desirable to have at least one “dedicated” acid deposition monitoring site within an area that represents a lower loading condition than what would exist near important source emitting areas. Together these dedicated monitoring sites would take necessary air pollutant and meteorological measurements for estimating dry deposition. The results would be used to represent a range of acid deposition loading conditions across a monitored area.

A tendency may exist to locate multiple “dedicated” acid deposition sites among important source emitting areas. However, state-of-the-art air dispersion models exist (e.g. CALPUFF) and can be used to show the potential variation in acid deposition loading at this local level. These models are not intended as a replacement for illustrating what is actually occurring in terms of dry (or wet) deposition within an airshed. However, such models offer an inexpensive way to obtain knowledge about how acid deposition loadings vary under ideal conditions at a small spatial scale within source emitting areas of interest.

4. To balance a desire to obtain additional field measurements, a *fourth important aspect* to consider for airshed network monitoring is using less-expensive passive monitors to gather integrated SO<sub>2</sub>/NO<sub>2</sub> concentration data from across the monitored area. This approach is already being used by the Wood Buffalo Environmental Association Terrestrial Environmental Effects Monitoring (TEEM) Program in the oil sands area north of Fort McMurray and by the West Central Airshed Society within the air monitoring area for power plants east of Edmonton.

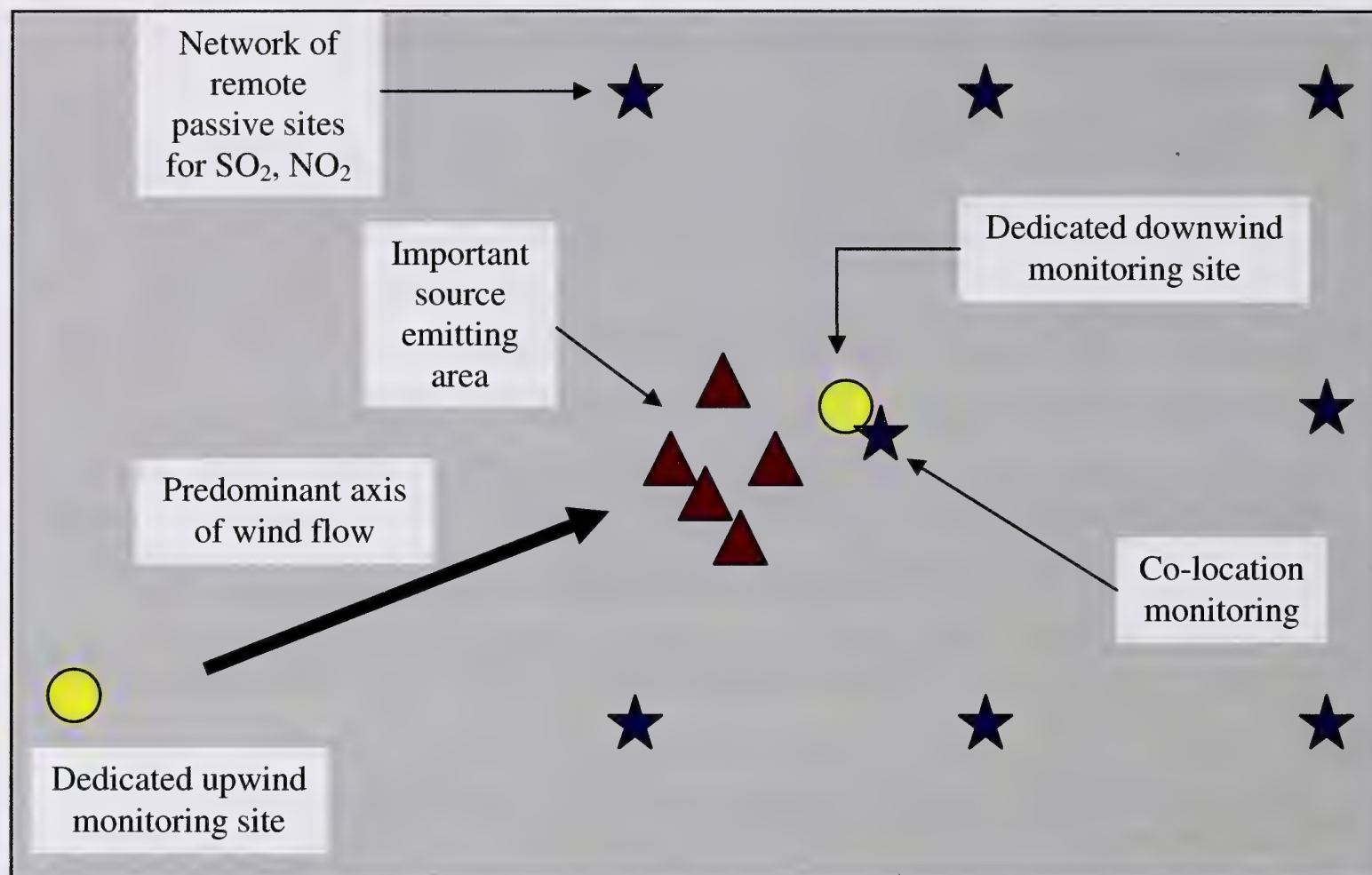
The approach is to deploy passive samplers to obtain integrated measurements of atmospheric gases (SO<sub>2</sub>, NO<sub>2</sub>) at remote sites across an airshed. Estimates of dry deposition can then be inferred for these gases at remote sites using meteorological parameter data from a “dedicated” acid deposition site within the airshed and making default assumptions for other parameters needed to estimate deposition velocity ( $V_d$ ). This approach will admittedly introduce uncertainty into dry deposition estimates at the remote sites, however a tradeoff is being made in costs for obtaining the data. In terms of concentration estimates at the remote sites, this uncertainty can partially be addressed by co-locating passive monitors at the “dedicated” acid deposition site for simultaneous measurement of atmospheric gases (SO<sub>2</sub>, NO<sub>2</sub>).

A number of acidic parameters would not be monitored at these remote sites using passive monitors, e.g. HNO<sub>3</sub>, HNO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and base cations – Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and K<sup>+</sup>. However, recently passive samplers have been used to monitor HNO<sub>3</sub> in remote forested areas of Sequoia National Park, California (Bytnerowicz et al., 2002) and may be useful in Alberta. This is described further in the next section.

The regional airshed network monitoring approach is depicted in Figure 8 using an upwind/downwind siting strategy for dedicated acid deposition monitoring sites (after US EPA 2001). Other siting strategies can be employed, as necessary, for the dedicated acid



deposition monitoring sites in order to document a range of acid deposition loading conditions across a monitored area. However, having an ability to establish trend information is essential and this fact may require that dedicated acid deposition monitoring sites be established and operated for up to five to ten years (or longer where emissions of acidic parameters continue to increase).



**Figure 8 Hypothetical layout of dry deposition monitoring network incorporating dedicated gaseous, particulate, and meteorological monitoring; and passive gas monitoring sites surrounding important source emitting area.**

## 3.2 Methodological Issues

A number of methodological issues are discussed below in relation to identifying whether the general approach, proposed above, can be put into practice for measuring and estimating dry deposition of acidic substances across airsheds in Alberta.

### 3.2.1 *Relationships of Dry Deposition for Sulphur and Nitrogen Species in Alberta*

One of the tasks attempted as part of the study was to estimate the contributions of  $\text{SO}_2$  and  $\text{NO}_2$  deposition in sulphur and nitrogen species deposition using available data. From a practical



point-of-view, if SO<sub>2</sub> and NO<sub>2</sub> deposition are dominant components of sulphur and nitrogen species deposition, simpler and less-expensive monitoring approaches – passive monitors – can be readily used to measure these gases at numerous remote sites in order to estimate deposition patterns in the airshed.

In order to examine this further, acidic and meteorological parameter data and estimates of sulphur and nitrogen species deposition were obtained from Alberta Environment for the Beaverlodge site (Figure 3). These data represented the period January 1998 to December 2002. These data were evaluated to calculate the ratio of annual gaseous SO<sub>2</sub> and NO<sub>2</sub> deposition to annual total sulphur and nitrogen species deposition. As indicated in Section 2.3.1, NO<sub>x</sub> was measured at the Beaverlodge site and it was used to represent NO<sub>2</sub> for this analysis. Results of the evaluation are presented below.

Annual sulphur and nitrogen species deposition at Beaverlodge site are summarized in Table 1 (expressed as kg species/ha/yr) and Table 2 (expressed as kg S or N/ha/yr) for the period 1998 to 2002.

**Table 1 Annual sulphur and nitrogen species deposition at Beaverlodge expressed as kg species/ha/yr.**

| Year | Gaseous parameters                               |                  |                  |                                    | Ions in Particulate Matter    |                              |                              |
|------|--|------------------|------------------|------------------------------------|-------------------------------|------------------------------|------------------------------|
|      | SO <sub>4</sub> <sup>2-</sup> as SO <sub>2</sub> | HNO <sub>2</sub> | HNO <sub>3</sub> | NO <sub>x</sub> as NO <sub>2</sub> | SO <sub>4</sub> <sup>2-</sup> | NH <sub>4</sub> <sup>+</sup> | NO <sub>3</sub> <sup>-</sup> |
|      | kg/ha/yr   | kg/ha/yr         | kg/ha/yr         | kg/ha/yr                           | kg/ha/yr                      | kg/ha/yr                     | kg/ha/yr                     |
| 1998 | 0.736  | 0.325            | 1.665            | 2.028                              | 0.250                         | 0.099                        | 0.135                        |
| 1999 | 0.610  | 0.170            | 2.170            | 1.826                              | 0.215                         | 0.077                        | 0.152                        |
| 2000 | 0.587  | 0.214            | 1.855            | 1.809                              | 0.191                         | 0.069                        | 0.130                        |
| 2001 | 0.633  | 0.327            | 2.700            | 1.880                              | 0.208                         | 0.064                        | 0.155                        |
| 2002 | 0.635  | 0.770            | 4.282            | 2.231                              | 0.217                         | 0.052                        | 0.180                        |

**Table 2 Annual sulphur and nitrogen species deposition at Beaverlodge expressed as kg S or N/ha/yr.**

| Year | Gaseous parameters                               |                  |                  |                                    | Ions in Particulate Matter    |                              |                              |
|------|--|------------------|------------------|------------------------------------|-------------------------------|------------------------------|------------------------------|
|      | SO <sub>4</sub> <sup>2-</sup> as SO <sub>2</sub> | HNO <sub>2</sub> | HNO <sub>3</sub> | NO <sub>x</sub> as NO <sub>2</sub> | SO <sub>4</sub> <sup>2-</sup> | NH <sub>4</sub> <sup>+</sup> | NO <sub>3</sub> <sup>-</sup> |
|      | kg S/ha/yr                                       | kg N/ha/yr       | kg N/ha/yr       | kg N/ha/yr                         | kg S/ha/yr                    | kg N/ha/yr                   | kg N/ha/yr                   |
| 1998 | 0.368  | 0.097            | 0.370            | 0.617                              | 0.083                         | 0.077                        | 0.030                        |
| 1999 | 0.305  | 0.051            | 0.482            | 0.556                              | 0.072                         | 0.060                        | 0.034                        |
| 2000 | 0.294  | 0.064            | 0.412            | 0.551                              | 0.064                         | 0.054                        | 0.029                        |
| 2001 | 0.317  | 0.098            | 0.600            | 0.572                              | 0.069                         | 0.050                        | 0.035                        |
| 2002 | 0.317  | 0.229            | 0.952            | 0.679                              | 0.072                         | 0.040                        | 0.041                        |



Using results from Table 2, the ratio of SO<sub>2</sub> deposition to total sulphur species deposition and of NO<sub>x</sub> deposition to total nitrogen species deposition were determined. These results are presented in Table 3 (SO<sub>2</sub> to total S species deposition ratio) and Table 4 (NO<sub>x</sub> to total N species deposition ratio), respectively.

**Table 3 Ratio of annual SO<sub>2</sub> deposition to total sulphur species deposition at Beaverlodge, Alberta.**

| SO <sub>4</sub> <sup>2-</sup> as SO <sub>2</sub> |            | SO <sub>4</sub> <sup>2-</sup> | SO <sub>2</sub> /S <sub>tot</sub> |             |
|--|------------|-------------------------------|-----------------------------------|-------------|
| Year   | kg S/ha/yr | kg S/ha/yr                    | 3.2.1.1                           | Ratio       |
| 1998   | 0.368      | 0.083                         |                                   | <b>0.82</b> |
| 1999   | 0.305      | 0.072                         |                                   | <b>0.81</b> |
| 2000   | 0.294      | 0.064                         |                                   | <b>0.82</b> |
| 2001   | 0.317      | 0.069                         |                                   | <b>0.82</b> |
| 2002   | 0.317      | 0.072                         |                                   | <b>0.81</b> |

$$\text{Note: } \frac{SO_2}{S_{tot}} \text{ Ratio} = \frac{SO_2}{SO_2 + SO_4^{2-}}$$

**Table 4 Ratio of annual NO<sub>x</sub> deposition to total nitrogen species deposition at Beaverlodge, Alberta.**

| HNO <sub>2</sub> |            | HNO <sub>3</sub> | NO <sub>x</sub> as NO <sub>2</sub> | NH <sub>4</sub> <sup>+</sup> | NO <sub>3</sub> <sup>-</sup> | NO <sub>x</sub> /N <sub>tot</sub> |             |
|------------------|------------|------------------|------------------------------------|------------------------------|------------------------------|-----------------------------------|-------------|
| Year             | Kg N/ha/yr | kg N/ha/yr       | kg N/ha/yr                         | kg N/ha/yr                   | kg N/ha/yr                   | 3.2.1.2                           | Ratio       |
| 1998             | 0.097      | 0.370            | 0.617                              | 0.077                        | 0.030                        |                                   | <b>0.52</b> |
| 1999             | 0.051      | 0.482            | 0.556                              | 0.060                        | 0.034                        |                                   | <b>0.47</b> |
| 2000             | 0.064      | 0.412            | 0.551                              | 0.054                        | 0.029                        |                                   | <b>0.50</b> |
| 2001             | 0.098      | 0.600            | 0.572                              | 0.050                        | 0.035                        |                                   | <b>0.42</b> |
| 2002             | 0.229      | 0.952            | 0.679                              | 0.040                        | 0.041                        |                                   | <b>0.35</b> |

$$\text{Note: } NO_x/N_{tot} \text{ Ratio} = \frac{NO_x}{NO_x + HNO_3 + HNO_2 + NH_4^+ + NO_3^-}$$

The above findings for S species (Table 3) indicate that consistently about 80% of annual S deposition was in the form of gaseous SO<sub>2</sub> with the remainder as particulate sulphate. These consistent results indicate that passive monitoring for gaseous SO<sub>2</sub> using passive monitors may be reasonable for representing total S species dry deposition.



Deposition results for N species indicate greater inconsistency. Deposition results for annual N species indicate greater inconsistency. The above findings for N species (Table 4) indicate that about 35 to 50% of N deposition is from NO<sub>x</sub> with the remainder as nitric and nitrous acid (~40 to 60%) and particulate ammonium and nitrate (~4 to 9%).

Peake and Davidson (1990) reported on calculated annual dry deposition of nitrogen species (NO<sub>x</sub>, HNO<sub>2</sub>, HNO<sub>3</sub>, and NO<sub>3</sub><sup>-</sup>) in the south western region of Alberta (Table 5). This region stretches east from the Great Divide of the Rocky Mountains to the plains of southern Alberta, 80 km east of Calgary, as discussed by Peake and Davidson (1990). These estimates were based upon measurements made at Crossfield east and west, and Fortress Mountain monitoring sites during 1985 to 1987 as part of the Alberta Government/Industry Acid Deposition Research Program (ADRP).

**Table 5 Ratio of annual NO<sub>x</sub> deposition to total nitrogen species deposition in the south western region of Alberta based upon measurements made at Crossfield east and west, and Fortress Mountain monitoring sites as part of the Alberta Government/Industry Acid Deposition Research Program (after Peake and Davidson, 1990).**

| HNO <sub>2</sub> | HNO <sub>3</sub> | NO <sub>x</sub> (NO + NO <sub>2</sub> ) | NO <sub>3</sub> <sup>-</sup> | NO <sub>x</sub> /N <sub>tot</sub> |             |
|------------------|------------------|---|------------------------------|-----------------------------------|-------------|
| Kg N/ha/yr       | kg N/ha/yr       | kg N/ha/yr                              | kg N/ha/yr                   | 3.2.1.3                           | Ratio       |
| 0.38             | 0.79             | 0.59                                    | 0.10                         |                                   | <b>0.31</b> |

Note:  $NO_x/N_{tot} \text{ Ratio} = \frac{NO_x}{NO_x + HNO_3 + HNO_2 + NO_3^-}$

Results presented in Table 5 tend to support findings presented in Table 4 indicating that about 32% of N deposition is from NO<sub>x</sub> (NO + NO<sub>2</sub>) with the remainder as nitric and nitrous acid (~63%) and particulate nitrate (~5%). Bytnerowicz et al. (1999) as cited in Bytnerowicz et al. (2005) reported that HNO<sub>3</sub> typically provides more than 60% of all dry-deposited N species in mixed conifer forests of the Los Angeles Basin mountain range. Thus these findings indicate that monitoring for gaseous NO<sub>2</sub> using passive monitors may substantially underestimate total annual N species dry deposition. Other N species deposition (e.g. HNO<sub>3</sub>) may be as or more important.

RWDI (2004) recently modeled relative deposition of nitrogen parameters (NO<sub>2</sub>, NO, HNO<sub>3</sub>, and NO<sub>3</sub><sup>-</sup>) in a large area surrounding oil sand development in northeastern Alberta using the CALPUFF air dispersion model. It was found that further away from source emitting areas, e.g. >50 km away, total NO<sub>2</sub> deposition loading (as kg N/ha/yr) was on the order of ten times greater than that predicted for HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup> deposition loadings expressed as kg N/ha/yr.



### 3.2.2 *Investigation of Nitric Acid Passive Sampler*

Nitric acid ( $\text{HNO}_3$ ) vapor is a principal component of dry acid deposition. Because of its high reactivity and deposition velocity,  $\text{HNO}_3$  provides large amounts of nitrogen deposition to ecosystems. For example, some studies have concluded that  $\text{HNO}_3$  typically contributes as much as 60% of all dry-deposited nitrogen (Bytnerowicz et al., 2005). Deposition of  $\text{HNO}_3$  can lead to eutrophication of sensitive ecosystems, contamination of surface waters with nitrate ( $\text{NO}_3^-$ ), and vegetation damage.

Information on  $\text{HNO}_3$  spatial and temporal distribution is critical for calculating nitrogen deposition at the local and regional scale. Determination of  $\text{HNO}_3$  concentrations is usually best conducted using integrated samplers, such as annular denuder systems (Possanzini et al., 1983) or honeycomb denuder systems (Koutrakis et al., 1993). Although precise, these systems are expensive, labor intensive and require a power supply.

*Soil Sampling.* A highly significant relationship between  $\text{HNO}_3$  concentrations and its accumulation in the upper layers of soils indicates that carefully prepared soil samples (especially clay fraction) may be useful as passive samplers for evaluation of ambient concentrations of  $\text{HNO}_3$  (Padgett and Bytnerowicz, 2001). These researchers found that the amount of extractable  $\text{NO}_3^-$  from isolated sand, silt, and clay fractions increased predictably with increasing atmospheric concentrations of  $\text{HNO}_3$  and duration of exposure. Their conclusions are that direct deposition, rather than biological processes (nitrogen cycling, biological uptake, and nutrient sequestration), is the causal agent for changes in surface concentrations of  $\text{NO}_3^-$  (Padgett and Bytnerowicz, 2001).

The application of this concept – sampling soils – for field scale assessment of  $\text{HNO}_3$  deposition loading still requires more experimental evaluation. Careful calibration of the technique in various environmental (e.g. cold temperature) conditions is needed. In addition, a better understanding of the relationship between moisture content, particle size, deposition, adsorption, potential revolatilization, and other factors needs to be developed. Given this understanding, one could calculate average atmospheric  $\text{HNO}_3$  concentration over specific time based on the sampling of carefully prepared soil samples (Padgett and Bytnerowicz, 2001). Even under controlled conditions, no other techniques using environmentally relevant materials such as leaf washing or surrogate surfaces have demonstrated such close correlations between atmospheric concentrations of  $\text{HNO}_3$  and its flux (Padgett and Bytnerowicz, 2001).

*Passive Sampling.* Passive (diffusive) samplers are an alternative to expensive, labor intensive integrated sampling systems. Passive samplers can measure average concentrations by being exposed at a selected site for an extended period (typically two to four weeks) and then subsequently being analyzed in a laboratory. Passive samplers are easy to use, inexpensive, and do not require a power supply so they can be deployed in large numbers at remote locations.

To avoid the problems of noise and bulk associated with annular denuder systems, a passive type of diffusive sampler was developed to monitor  $\text{HNO}_3$  concentrations inside museums (De Santis et al., 2003). These passive samplers are a modification of the open-tube design obtained by



using a filter treated with appropriate reagents to trap the pollutant. The body of the sampler is a cylindrical glass vial with a threaded cap at one end.

The pollutant is collected on an impregnated disc placed at the bottom of the vial and held in position by a stainless steel ring. To avoid turbulent diffusion inside the vessel, the open end is protected using a fine stainless steel screen. At the end of the exposure period the sampler is capped and returned to a laboratory for analysis. Although these samplers were designed for indoor use, the developers have attempted to use them outdoors with some success for short-term periods under controlled conditions (De Santis et al., 2003).

Generic diffusion passive samplers have been successfully employed for limited durations to determine outside concentrations of  $\text{HNO}_3$  (Lan et al., 2004). In addition, Bytnerowicz et al. (2001) developed a simple and inexpensive passive sampler specifically designed for monitoring ambient concentrations of  $\text{HNO}_3$ . Recently, this sampler has been improved to provide quantitative and reliable measurements even under strong wind conditions (Bytnerowicz et al., 2005). This new generation sampler may well represent a proven and reliable passive sampler available for ambient measurements of  $\text{HNO}_3$ .

Passive samplers have been employed recently to determine outside concentrations of  $\text{HNO}_3$  (Lan et al., 2004). In general, passive samplers work via diffusion of a contaminant from an area of high concentration in air to an area of low concentration on the passive sampler. The contaminant is then trapped on an impregnated filter at the end of the diffusion path. The passive samplers consist of four main parts: a collecting filter impregnated with an appropriate reagent, a vessel that can serve as a container and a diffusion part, a filter or mesh for preventing penetration of particles and water, and a cap with open holes through which the ambient air containing pollutants diffuses.

The impregnating agent and filter type depend on the contaminant, and in the case of  $\text{HNO}_3$ , a NaCl and glycerin aqueous reagent solution is used on a cellulose filter (Lan et al., 2004). Once exposed for durations of up to one month, the collected  $\text{HNO}_3$  is extracted using water and analyzed as  $\text{NO}_3^-$ . The concentration of  $\text{HNO}_3$  in air is estimated knowing the amount of gas collected on the filter, exposure time, and a conversion coefficient. The conversion coefficient is established by measuring the concentration of  $\text{HNO}_3$  in the same area over the same duration using a filter pack (Lan et al., 2004).

United States Department of Agriculture (USDA) Forest Service and University of California researchers have developed a simple and inexpensive passive sampler for monitoring air concentrations of  $\text{HNO}_3$  (Bytnerowicz et al., 2001). The sampler is based on diffusion of ambient air through a Teflon membrane and absorption of pollutants on a Nylasorb nylon filter. The sampler is simple in design, easy to make, inexpensive, and resistant to harsh weather conditions (Bytnerowicz et al., 2001).

$\text{HNO}_3$  is selectively absorbed on 47-mm Nylasorb nylon filters with no interference from particulate  $\text{NO}_3^-$  (Bytnerowicz et al., 2001). Concentrations determined with the passive samplers closely corresponded with those measured with collocated honeycomb annular denuder systems both in ambient conditions and in controlled  $\text{HNO}_3$  exposures (Bytnerowicz et al.,



2001). A PVC protective cap is used to protect the nylon filters from rain and wind and allow for reliable measurements of ambient  $\text{HNO}_3$  concentrations. The described samplers have been successfully deployed in Sequoia National Park (Bytnerowicz et al., 2002a), San Bernardino Mountains (Alonso et al., 2002), and on Mammoth Mountain in California (Bytnerowicz et al., 2002b).

After use of these samplers in the field over long durations in different conditions it was the researchers' conclusion that precision of the  $\text{HNO}_3$  passive samplers could be improved if a diffusion barrier providing uniform flow of air to the collection medium was installed in the samplers (Bytnerowicz et al., 2002a). The reason for this is that at high wind speeds typical of high elevation mountains, laminar airflow controlling  $\text{HNO}_3$  deposition to the sampler nylon filters could be affected by uncontrolled turbulent flow. In such conditions a consistent quantitative measurement of the pollutant would not be possible. Therefore a need for developing a new sampler that would assure quantitative and reliable measurements even under strong winds became evident.

The new generation passive sampler is more precise than the old open-face  $\text{HNO}_3$  sampler (Bytnerowicz et al., 2005). It can measure wide ranges of ambient  $\text{HNO}_3$  concentrations for extended periods of time and can be used for regional-scale monitoring of the pollutants. Just as the prototype sampler, nylon filters of 47-mm diameter are used as a collection medium for  $\text{HNO}_3$  (in addition to  $\text{HNO}_2$ ). Ambient air passes to the nylon filter through a Teflon 47-mm diameter filter of 2  $\mu\text{m}$  pore size. The filters are housed in a 50-mm commercially available polycarbonate Petri dish and are kept in place by two Teflon rings and one PVC ring. The samplers are protected from wind and rain by a polycarbonate cap (Figure 9) (Bytnerowicz et al., 2005).

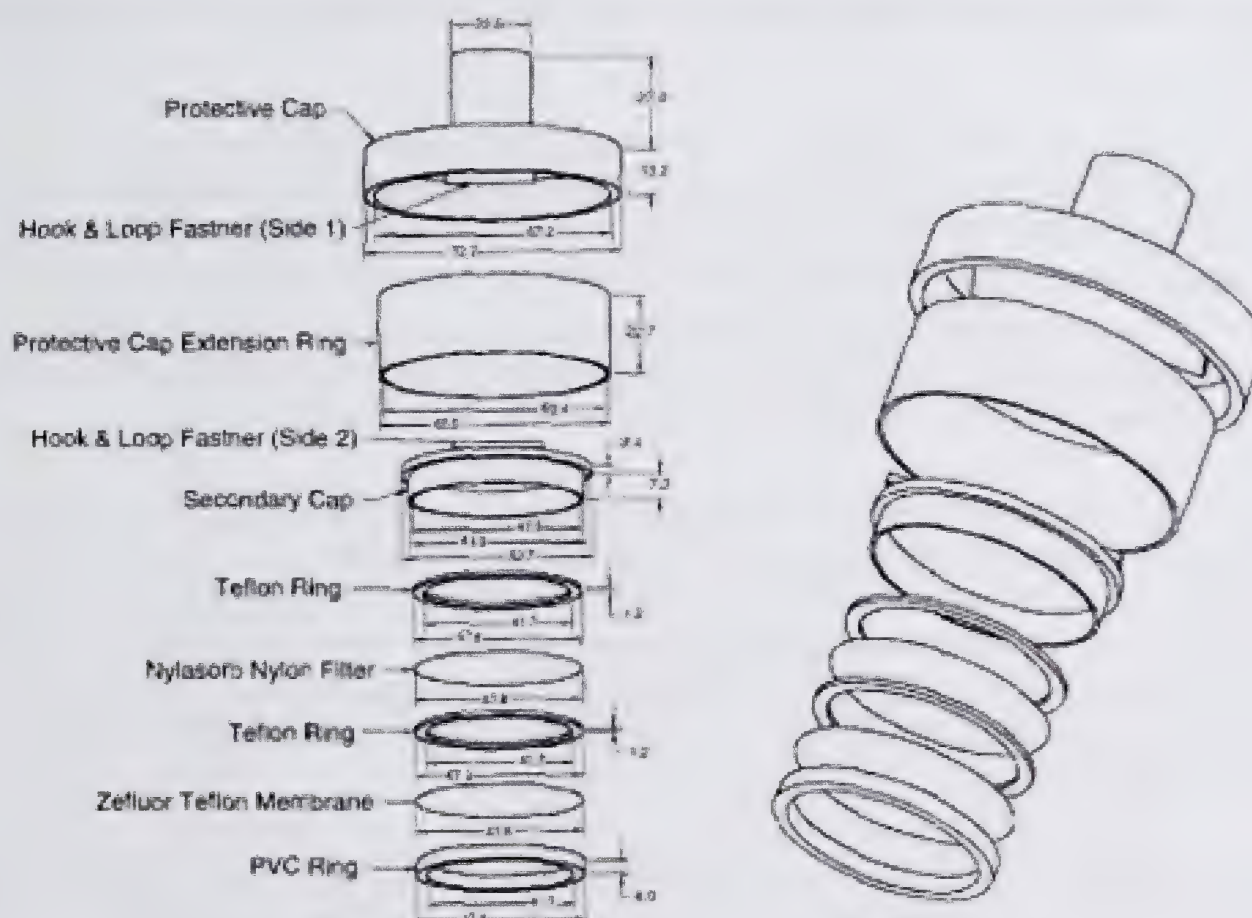
After exposure, the nylon filters are placed in 250-mL Erlenmeyer flasks into which 0.02 L of distilled/deionized water is added. The amount of absorbed gases as  $\text{NO}_3^-$  is subsequently determined using an ion exchange chromatograph and expressed as micrograms  $\text{NO}_3^-$ /filter. Concentrations of  $\text{HNO}_3$ ,  $\text{HNO}_2$ , and total  $\text{HNO}_3$  and  $\text{HNO}_2$  can then be calculated using known linear relationships between total  $\text{NO}_3^-$ /filter and ambient concentrations of the pollutant measured using denuder calibration systems in the same area. Concentrations can then be expressed as  $\mu\text{g}/\text{m}^3$ .

The precision of the new sampler is higher than that of the open-face  $\text{HNO}_3$  sampler (Bytnerowicz et al., 2005). However, there is some indication that perhaps in ambient air significant amounts of  $\text{HNO}_3$  are lost on the Teflon pre-filter. Bytnerowicz et al. (2005) indicated that this could result from absorption of  $\text{HNO}_3$  on particulate matter collected on the pre-filter or water condensing on it during cool and moist conditions (typically during night and early morning hours). Performance of the sampler in conditions of high-dust pollution or high relative humidity may therefore be impaired.

Further testing would be required to better understand the significance of this potential problem. Careful calibrations against denuder systems or other reference methods should be performed in the areas of interest in various seasons. This is because of the above mentioned potential interferences caused by dust particles and high humidity and also  $\text{HNO}_2/\text{HNO}_3$  ratios change in



time and space depending on activity of ambient photochemical processes. Information on individual concentrations of  $\text{HNO}_3$  and  $\text{HNO}_2$  is also very important from points of view of improved understanding air chemistry, long-range distribution of pollution plumes, and potential toxic and phytotoxic effects (Bytnerowicz et al., 2005).



**Figure 9. Schematic of the  $\text{HNO}_3$  passive sampler (after Bytnerowicz et al., 2005).**

### **3.2.3 Use of Meteorological Data for Estimating Dry Deposition**

Another issue that exists is identifying a suitable averaging time period for meteorological data that are used for estimating the resistance terms ( $R_a$ ,  $R_b$ , and  $R_c$ ) and the corresponding deposition velocity ( $V_d$ ) for acidic parameters. This issue is related to calculations with parameter concentrations that are measured with longer-term monitoring periods, e.g. denuders or passive monitors with weekly, bi-weekly, or monthly sample deployments.

Meteorological data and gas and particulate concentration data need to be at the same time interval to enable calculations of deposition velocity and deposition. The notion is that shorter time-resolved meteorological data can be averaged out and combined with longer time-averaged air concentration data from integrated monitors to calculate dry deposition. Meteorological factors representing atmospheric turbulence and stability are important factors influencing the aerodynamic ( $R_a$ ) and boundary-layer ( $R_b$ ) resistance terms in Equation 1. Atmospheric



turbulence and stability tend to exhibit a diurnal variation. For example, during nighttime the atmosphere tends to be stable and during daytime it tends to be unstable. A result is that averaging out meteorological factors over much longer, e.g. weekly, bi-weekly, or monthly periods, may not capture these variations and introduce uncertainty in calculation of the resistance terms and corresponding dry deposition estimates.

The current approach uses short averaging time periods for meteorological data for estimating resistance terms:

- CASTNet sites operated by the US Environmental Protection Agency (Clarke et al., 1997) use hourly-average meteorological observations for estimating resistance terms. The deposition velocity ( $V_d$ ) for each chemical species and major vegetation surface type is estimated for each hour. The deposition velocity for a site is then calculated as an area-weighted  $V_d$  over vegetation types within 1 km of a site. Hourly deposition velocity values are then averaged over a week and multiplied by weekly-integrated concentrations to produce weekly deposition loadings of  $\text{HNO}_3$ ,  $\text{SO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_2$ .
- Alberta Environment has used 1-hour average values of meteorological observations for estimating the resistance terms in estimating dry deposition at former acid deposition monitoring sites (Aklilu, 1999; Bates, 1996). For example, for a typical 31-day month  $31 \times 24 = 744$  different hourly meteorological observations are used to compute a similar number of hourly average deposition velocities and deposition loadings for each acidic parameter. A monthly deposition load would be computed by summing the individual hourly average loadings.
- Both Wood Buffalo Environmental Association (EPCM, 2002) and West Central Airshed Society (Scotten, 2004) have used 15-minute average values of meteorological observations for estimating the resistance terms. For example, for a typical 31-day month  $31 \times 24 \times 4 = 2,976$  different 15-minute meteorological observations are used to compute a similar number of 15-minute average deposition velocities and deposition loadings for each acidic parameter. A monthly deposition load would be computed by summing the individual 15-minute average loadings.

Calculations were undertaken in order to examine the effect of combining meteorological data and gas and particulate concentration data as monthly time interval values in order to estimate deposition velocity and deposition loading for that interval. Gaseous  $\text{SO}_2$  and meteorological data from Beaverlodge, Alberta for the periods: i) January 1998 to December 1998, and ii) January 1999 to December 1999 were used. These data were evaluated to calculate and compare deposition calculated as a “monthly average” versus deposition calculated as an “hourly average and summed over a month.” Results are presented in Tables 6 and 7, and Figures 10 and 11, respectively for the 1998 and 1999 data.

Table 6 and Figure 10 indicate that estimating  $\text{SO}_2$  gaseous deposition based on calculating “monthly-average” gaseous  $\text{SO}_2$  and meteorological values compares well to deposition based on an “hourly average and summed over a month.” Table 6 shows the % variation in the annual



load for the “monthly average” approach was within 8% of the “hourly average” (current) approach.

Table 7 and Figure 11 also indicate that estimating SO<sub>2</sub> gaseous deposition based on calculating “monthly-average” gaseous SO<sub>2</sub> and meteorological values compares well to deposition based on an “hourly average and summed over a month.” Table 7 shows the % variation in the annual load for the “monthly average” approach was within 4% of the “hourly average” (current) approach.

**Table 6 SO<sub>2</sub> gaseous deposition for 1998 at Beaverlodge, AB - deposition calculated as a monthly average versus current approach (deposition calculated as an hourly average and summed over a month) (kg/ha as SO<sub>2</sub>).**

| Month     | Hourly | Monthly | % Variation* |
|-----------|--------|---------|--------------|
| January   | 0.0594 | 0.0604  | 2            |
| February  | 0.0704 | 0.0753  | 7            |
| March     | 0.0915 | 0.1069  | 17           |
| April     | 0.0231 | 0.0293  | 27           |
| May       | 0.0261 | 0.0257  | -2           |
| June      | 0.0788 | 0.0850  | 8            |
| July      | 0.0597 | 0.0582  | -3           |
| August    | 0.0582 | 0.0558  | -4           |
| September | 0.0824 | 0.0811  | -2           |
| October   | 0.0632 | 0.0909  | 44           |
| November  | 0.0469 | 0.0504  | 7            |
| December  | 0.0767 | 0.0753  | -2           |
| Annual    | 0.7364 | 0.7943  | 8            |

\* % variation relative to hourly average deposition velocity summed over a month;  

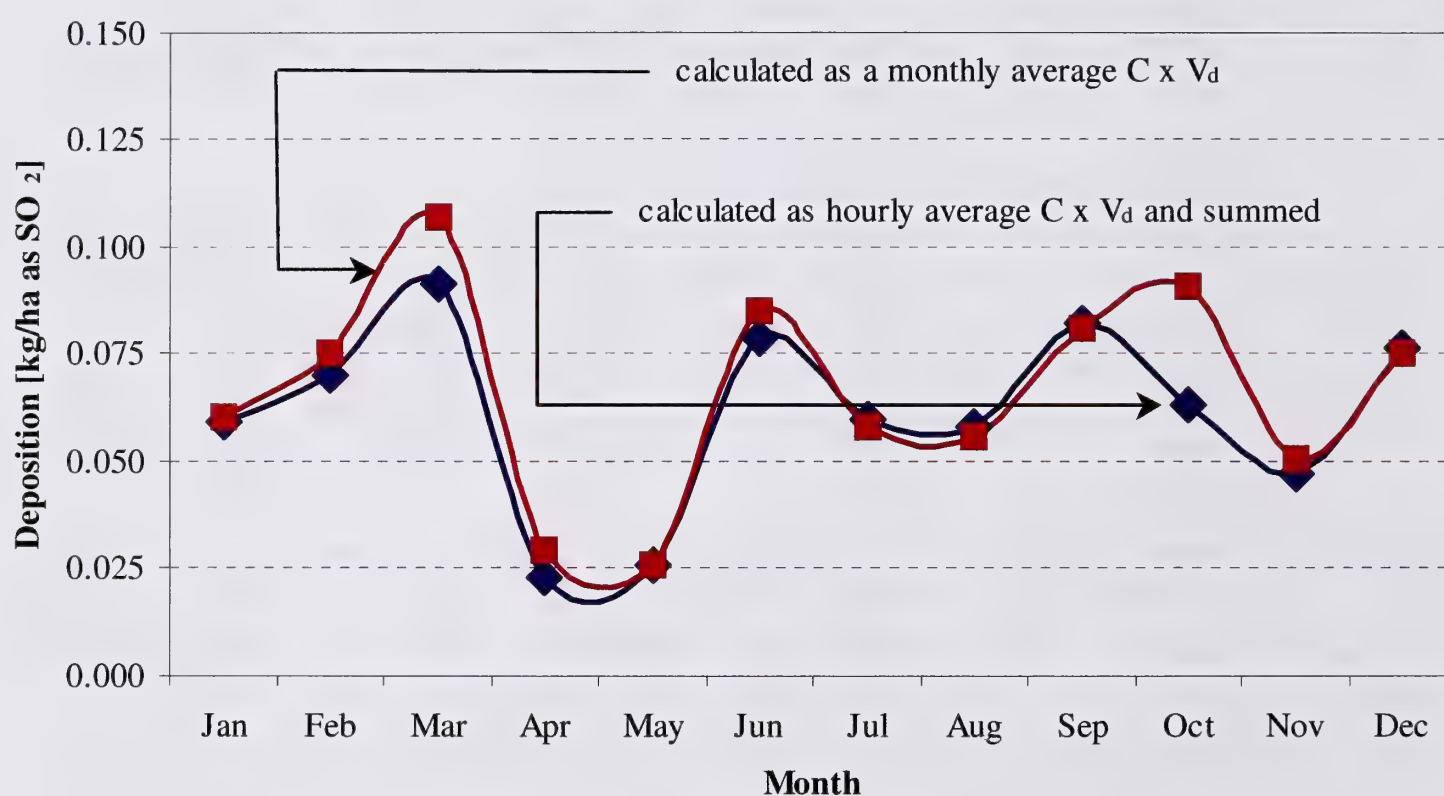
$$= \frac{\text{Monthly} - \text{Hourly}}{\text{Hourly}} \times 100\%$$

Estimating deposition velocity and loadings by computing longer-term – monthly – average meteorological and concentration values result in minor differences in annual dry deposition rates. In comparing the two approaches in Figures 10 and 11, no obvious visual trend can be observed in looking at month-to-month variations. While both approaches are resource intensive, they are readily handled with today’s computing software capabilities.



### 3.2.4 Co-location Monitoring

In order to better understand the spatial relationship among acidic parameters within an airshed, deployment of passive samplers across the airshed (including at dedicated acid deposition monitoring sites within the airshed) could be performed. The intent of this approach is to gather information on potential relationships between acidic parameters (i.e.  $\text{SO}_2$  versus total S deposition and  $\text{NO}_2$  versus total N deposition) and on deposition patterns within a local area of the airshed. Two of the airshed zones in Alberta currently or will have this monitoring arrangement to gather information on acidic parameters, West Central Airshed Society and Wood Buffalo Environmental Association. These are described further below.



**Figure 10 Monthly average  $\text{SO}_2$  gaseous deposition for 1998 at Beaverlodge, AB – deposition calculated as a monthly average versus current approach (deposition calculated as an hourly average and summed over a month).**



**Table 7 SO<sub>2</sub> gaseous deposition for 1999 at Beaverlodge, AB - deposition calculated as a monthly average versus current approach (deposition calculated as an hourly average and summed over a month) (kg/ha as SO<sub>2</sub>).**

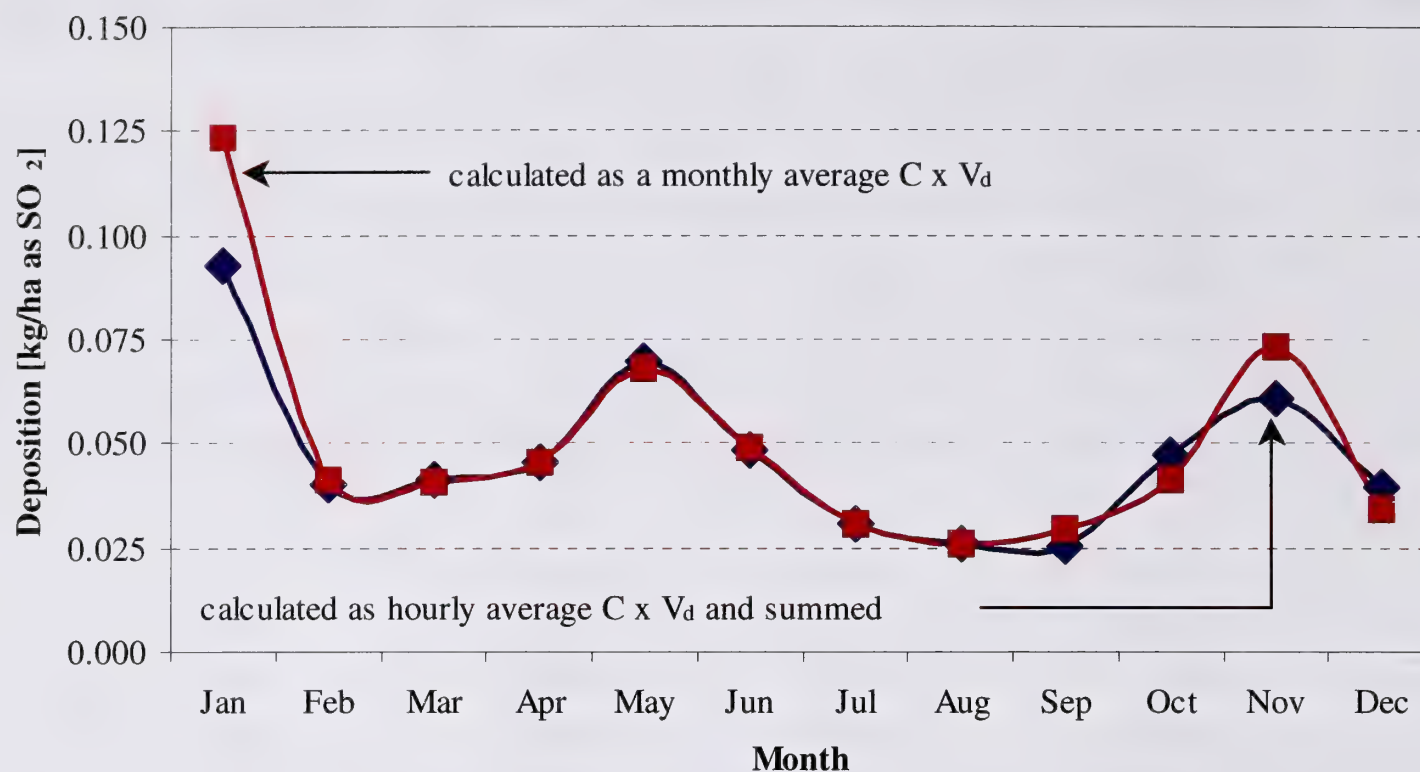
| Month     | Hourly | Monthly | % Variation* |
|-----------|--------|---------|--------------|
| January   | 0.0927 | 0.1232  | 33           |
| February  | 0.0403 | 0.0416  | 3            |
| March     | 0.0414 | 0.0409  | -1           |
| April     | 0.0453 | 0.0454  | 0            |
| May       | 0.0694 | 0.0682  | -2           |
| June      | 0.0486 | 0.0489  | 1            |
| July      | 0.0305 | 0.0306  | 0            |
| August    | 0.0262 | 0.0260  | -1           |
| September | 0.0254 | 0.0296  | 17           |
| October   | 0.0475 | 0.0412  | -13          |
| November  | 0.0607 | 0.0730  | 20           |
| December  | 0.0393 | 0.0340  | -13          |
| Annual    | 0.5673 | 0.6026  | 4            |

\* % variation relative to hourly average deposition velocity summed over a month;

$$= \frac{\text{Monthly} - \text{Hourly}}{\text{Hourly}} \times 100\%$$

**West Central Airshed Society (WCAS)** – Arrangements have been made with WCAS and power plant operators (EPCOR and TransAlta) to allow all relevant acid deposition data collected from their program described in Section 2.3.2 – dedicated acid deposition monitoring site and rural passive (SO<sub>2</sub>, NO<sub>2</sub>) monitoring network – to be compiled after a one-year period and passed on to Alberta Environment for evaluation purposes. The anticipated timing of receipt of these data is spring 2006.

**Wood Buffalo Environmental Association** – Efforts were made to implement collocation of SO<sub>2</sub> and NO<sub>2</sub> passive samplers at their dedicated acid deposition monitoring site (Air Monitoring Station #1 – Fort McKay) to coincide with the TEEM passive monitoring program in late fall 2004 and early winter 2005. The current status of monitoring programs at Air Monitoring Station #1 (and other stations operated by WBEA) is under evaluation by the WBEA Air Monitoring Technical Committee (AMTC). Efforts have been unsuccessful in collocation of SO<sub>2</sub> and NO<sub>2</sub> passive samplers at this station because of this situation.



**Figure 11 Monthly average  $SO_2$  gaseous deposition for 1999 at Beaverlodge, AB – deposition calculated as a monthly average versus current approach (deposition calculated as an hourly average and summed over a month).**



## 4.0 DISCUSSION

### 4.1 Review of Methods

Routine dry deposition monitoring is not undertaken extensively throughout Alberta. Specifically, only two areas of the province have developed on-going dry deposition monitoring programs – the area where four power plants operate east of Edmonton (West Central Airshed Society) and the oil sands producing area (Wood Buffalo Environment Association). Both of these monitoring programs were reviewed, along with dry deposition monitoring procedures formerly used by Alberta Environment and corresponding dry deposition results. In addition, general descriptions of dry deposition monitoring approaches used by Environment Canada (Canadian Air and Precipitation Monitoring Network – CAPMoN) and US EPA (Clean Air Status and Trends Network – CASTNet) were reviewed.

No clear standard method for field measurement and estimation of dry deposition of acidic parameters exists. This is apparent as all of the field measurement methods vary to some degree with respect to the type of equipment (staged filter packs) for measuring selected acidic parameters ( $\text{HNO}_3$ ,  $\text{HNO}_2$ ,  $\text{NH}_3$ , and ions in suspended particulate matter). Field measurement methods for CAPMoN and CASTNet are consistent within each network and allow for comparisons of dry deposition data across each network. Both networks incorporate the inference method for estimation of dry deposition of acidic parameters with variations of the Leaf Area Index approach for estimating surface resistance ( $R_c$ ). Other specific relationships and estimation procedures used in CAPMoN and CASTNet for estimating dry deposition were not available based on the information reviewed.

Both airshed organizations in Alberta use annular denuder samplers for measuring selected acidic parameters ( $\text{HNO}_3$ ,  $\text{HNO}_2$ ,  $\text{NH}_3$ ):

- WCAS uses integrated monitoring consecutively using a monthly sampling duration (that is to say the samplers draw air for a monthly period). This equates to 12 integrated samples collected over a year representing 100% of the ambient conditions occurring.
- WBEA uses integrated monitoring for one 24-hour period every 6<sup>th</sup> day. This equates to 61 integrated samples collected over a year, however only representing 1-in-6 days (17%) of the ambient conditions.

Both airshed organizations use integrated monitoring (one 24-hour integrated sample every 6<sup>th</sup> day) for measuring selected ions in particulate matter:

- WCAS collects TSP for analysis.
- WBEA collects  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  for analysis.

The particle-associated parameters derived from erosion of soil or plant material ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) tend to reside on larger airborne particles (e.g.  $>2\ \mu\text{m}$ ) (Lovett, 1994). The majority of airborne mass of  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}^+$  reside on submicrometer aerosols. Thus collecting  $\text{PM}_{10}$  or larger-sized airborne particles (TSP) provide more efficient capture of particle-associated parameters derived from erosion of soil or plant material.



The two calculation approaches for estimating dry deposition of gases in Alberta are those used by Alberta Environment (Appendix I) and those used by WBEA (Appendix I and Appendix II – Leaf Area Index approach). Both approaches appear reasonable in that estimates of deposition loading and velocities can be derived for gases. An attempt was made as part of this study to analyze how these approaches compared based upon using a similar dataset of from WCAS and WBEA. It was not possible to obtain a complete set of input pollutant concentration and meteorological data from these airshed organizations to perform the calculations. However, as indicated in Section 3.2.3, arrangements have been made with WCAS and power plant operators (EPCOR and TransAlta) to allow all relevant acid deposition and meteorological data from their on-going monitoring program to be compiled after a one-year period and passed on to Alberta Environment for evaluation purposes.

## **4.2 Components of Dry Deposition Network**

The two areas of the province that have developed routine dry deposition monitoring programs – WCAS and WBEA – are in response to determining the influence of multiple emitting sources and activities in their respective airsheds. In the absence of such sources and activities, a monitoring site would be selected that measures “regional” deposition (i.e. some sort of average of what happens in the area, not “hotspots” from particular sources) (US EPA, 2001).

In the presence of multiple sources, components of a dry deposition network should include:

- A monitoring site that captures representative local influences of emission sources. Such a monitoring site is used to characterize the influence of local emissions. Consequently, at least one “dedicated” acid deposition monitoring site should be located near important source emitting areas to take necessary air pollutant and meteorological measurements for estimating dry deposition close to the sources.
- Having an ability to detect variation within a monitored area when using monitoring techniques for which no standard methods exist. In this situation it is desirable to have at least one “dedicated” acid deposition monitoring site within an area that represents a lower loading condition than what would exist near important source emitting areas. Together these dedicated monitoring sites would take necessary air pollutant and meteorological measurements for estimating dry deposition. The results would be used to represent a range of acid deposition loading conditions across a monitored area that takes into account a location influenced by local emission sources (e.g. downwind) and a representative area located further away (e.g. upwind).
- Additional information on spatial variation in dry deposition should also be sought across a monitored area. Here, less-expensive passive monitors can be used to gather integrated data for SO<sub>2</sub> and NO<sub>2</sub> across the monitored area (i.e. at remote site locations). As discussed in this report, this approach is already being used by the WBEA Terrestrial Environmental Effects Monitoring (TEEM) Program in the oil sands area north of Fort McMurray and by WCAS within the air monitoring area for power plants east of Edmonton. This approach will admittedly introduce uncertainty into dry deposition



estimates for total N species at remote sites as selected parameters that may be as more important (e.g.  $\text{HNO}_3$ ) would not be monitored. However a tradeoff is being made in costs for obtaining information on dry deposition for at least some acidic parameters (i.e.  $\text{SO}_2$  and  $\text{NO}_2$ ).

- Passive monitoring of  $\text{HNO}_3$  and  $\text{HNO}_2$  has been recently developed and used in the field by others in warmer climates of California (Bytnerowicz et al., 2005). If such an approach were to be considered in Alberta, field testing would be required to calibrate the monitors against a reference method (e.g. denuder system) during various seasons to better understand its capabilities, particularly in cold climates.

### 4.3 Monitoring of Acidic and Meteorological Parameters

An opportunity exists to develop a more formal network for monitoring dry deposition in Alberta airsheds that places greater emphasis on using consistent procedures for measuring and calculating dry deposition of acidic parameters. Specifically, this relates to:

- The type of acidic and meteorological parameters to measure.
- The frequency and duration in which the selected parameters are measured.
- The quantitative relationships and corresponding assumptions for selected parameters used to calculate dry deposition rates.

As most of the monitoring is currently undertaken by airshed organizations in Alberta, it makes sense to present these organizations with an approach that is practical, reasonably cost-effective, and takes into account site-specific information needs. With this in mind, these organizations should make better attempts at standardizing their monitoring procedures in terms of frequency and duration for both acidic parameters and meteorological parameters. An example of a consistent monitoring approach for the airsheds to consider is presented below, which should be comparable to or more cost-effective than the current approaches used:

#### 1. Acidic parameters:

- Atmospheric gases –
  - continuous monitoring of  $\text{SO}_2$  and  $\text{NO}_2$  at “dedicated” acid deposition monitoring sites (one site selected to represent influences near important source emitting areas and one site selected to represent influences in the airshed distant from important source emitting areas)
  - monthly or twice-monthly integrated annular denuder monitoring for  $\text{HNO}_2$ ,  $\text{HNO}_3$  (and  $\text{NH}_3$  if desired) at “dedicated” acid deposition monitoring sites
  - monthly integrated passive sampler monitoring of  $\text{SO}_2$  and  $\text{NO}_2$  at multiple sites across a monitored area
- Particulate matter parameters at “dedicated” acid deposition monitoring sites (these parameters can be obtained from filter samples included in annular denuder or VAPs sampling or they can be obtained separately from particulate matter sampling equipment (e.g.  $\text{PM}_{10}$  or TSP 24-hour integrated samples collected every 6<sup>th</sup> day) –
  - $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$

2. Meteorological parameters at dedicated “acid deposition” monitoring sites:
  - Monitoring and reporting of hourly or 15-min average values for:
    - Wind speed and wind speed standard deviation
    - Wind direction and wind direction standard deviation
    - Solar radiation
    - Relative humidity
    - Surface wetness
    - Air temperature at standard height (10 m)
    - Difference in air temperature at standard height and surface (taken as 2 m above ground).

#### **4.4 Relationships for Calculating Dry Deposition Loadings**

The importance of presenting transparent quantitative relationships (such as those relationships described in Appendix I) associated with dry deposition calculations is noted. A number of organizations have or currently monitor and report dry deposition (Alberta Environment, West Central Airshed Society, Wood Buffalo Environmental Association, Environment Canada, US Environmental Protection Agency).

The precise relationships used by West Central Airshed Society and Wood Buffalo Environmental Association could not be identified and documented as part of this study. In addition, review of scientific literature did not provide much clarity in the quantitative relationships used by Environment Canada and US Environmental Protection Agency other than to indicate that the relationships used have changed over time. In order for there to be consistency in performing dry deposition calculations over time, it is essential that transparent quantitative relationships be presented and used.

Estimating dry deposition requires collecting data on meteorological parameters described above. These meteorological data and gas and particulate concentration data need to be at the same time interval to enable calculations of deposition velocity and deposition. Meteorological data are recorded as hourly average or 15-min. average (in the case of WCAS and WBEA) or hourly (in the case of Alberta Environment) values. The current approach used for calculating deposition and deposition velocity is to recalculate gas and particulate concentration at the same time interval as meteorological data (hourly).

Calculations undertaken to examine the effect of combining meteorological data and gaseous SO<sub>2</sub> concentration data from Beaverlodge, Alberta as monthly time interval values resulted in minor differences in annual dry deposition rates (<8% variation) compared to deposition calculated as hourly average values and summed over a month. While both approaches are resource intensive, they are readily handled with today’s computing software capabilities.



## 4.5 Importance of Trends

Deposition rates of acidic parameters vary monthly and seasonally within a given year due to changes in meteorology and surface conditions. The importance of meteorological variation cannot be ignored. For example, deposition rates during a dry or a particularly wet year may not be representative of what generally happens at a monitored location. Because of this variability in deposition rates from year to year, a dry deposition monitoring program should be active for at least 3 to 5 years to get good data on average annual deposition rates to know if rates are similar or different from year to year.

Where emissions of acidic parameters to the atmosphere remain constant from sources within a region over long timeframes (i.e. 10 years or more), it should be reasonable to monitor dry deposition for 3 to 5 years (as indicated above) to document deposition characteristics. After dry deposition rates have been established, it should be possible to suspend monitoring for a number of years (e.g. 3 to 5 years) in the interests of costs. Over the longer term it is still important to establish whether longer-term changes are occurring (i.e. trends). Dry deposition monitoring should then be repeated for at least another 3 to 5 years to get good data on average annual deposition rates and to know if rates are changing over a longer timeframe.

Where emissions of acidic parameters to the atmosphere changes every couple of years from sources within a region, it is reasonable to anticipate changes to dry deposition loadings in the region. Here it is necessary to make longer commitments to more-routine dry deposition monitoring of acidic parameters in order to get good data on average annual deposition rates in relation to changes in source emissions (i.e. trend information).

## 5.0 FINDINGS

1. Components of a dry deposition network in the presence of multiple important emitting sources within a region should include:
  - Dedicated monitoring at a site to capture representative local influences of N and S species deposition.
  - Dedicated monitoring at a site representing lower N and S species deposition than what would exist near important source emitting areas.
  - Information on spatial variation of N and S species deposition within a region using less-expensive passive monitors. This approach will admittedly introduce uncertainty into dry deposition estimates as selected acidic parameters would not be monitored. However a tradeoff is being made in costs for obtaining information on dry deposition for at least some acidic parameters (e.g. SO<sub>2</sub>, NO<sub>2</sub>).
2. Passive monitoring of HNO<sub>3</sub> and HNO<sub>2</sub> has been recently developed and used in warmer climates. If such an approach were to be considered in Alberta, field testing would be required to calibrate the monitors against a reference method to better understand its capabilities in cold climates.
3. As most dry deposition monitoring is currently undertaken by airshed organizations in Alberta, it makes sense to present these organizations with an approach that is practical, reasonably cost-effective, and takes into account site-specific information needs. With this in mind, these organizations should make better attempts at standardizing their monitoring procedures in terms of frequency and duration for both acidic parameters and meteorological parameters. The opportunity exists to develop a more formal network for monitoring dry deposition in Alberta airsheds that places greater emphasis on using consistent procedures for measuring and calculating dry deposition of acidic parameters. Specifically, this relates to:
  - The type of acidic and meteorological parameters to measure.
  - The frequency and duration in which the selected parameters are measured.
  - The quantitative relationships and corresponding assumptions for selected parameters used to calculate dry deposition rates.
4. Passive monitoring of SO<sub>2</sub> may be an acceptable approach for representing total S species dry deposition at remote locations within a region using the assumption of similar meteorological characteristics measured at dedicated monitoring sites. Estimates of annual S species deposition for the Alberta Environment Beaverlodge site during 1998 to 2002 indicated that consistently about 80% of S deposition was in the form of gaseous SO<sub>2</sub> with the remainder as particulate sulphate.
5. This was not the case for passive monitoring of NO<sub>2</sub>. Passive monitoring does not appear to be an acceptable approach for representing total N species dry deposition at remote locations within a region using the assumption of similar meteorological characteristics measured at dedicated monitoring sites. Other N species deposition, e.g. HNO<sub>3</sub>, may be as or more important. Estimates of annual N species deposition for the Alberta Environment



Beaverlodge site during 1998 to 2002 indicated that ~35 to 50% of N deposition was from  $\text{NO}_x$  with the remainder as  $\text{HNO}_3$  and  $\text{HNO}_2$  (~40 to 60%) and particulate ammonium and nitrate (<10%). Estimates of annual N species deposition in the south western region of Alberta reported as part of the Alberta Government/Industry Acid Deposition Research Program during 1985 to 1987 indicated that ~32% of N deposition was from  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) with the remainder as nitric and nitrous acid (~63%) and particulate nitrate (~5%). This is consistent with findings for the Alberta Environment Beaverlodge site during 1998 to 2002.

6. Calculations undertaken to examine the effect of combining meteorological data and gaseous  $\text{SO}_2$  concentration data from Beaverlodge, Alberta as monthly time interval values tended to demonstrate similar deposition loadings. Annual 1998 and 1999  $\text{SO}_2$  deposition loadings based on computing monthly-average gaseous  $\text{SO}_2$  and meteorological values were within 8% of the current approach (deposition calculated as hourly average values and summed over a month). While both approaches are resource intensive, either are readily handled with today's computing software capabilities.

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## **APPENDIX I**

### **Alberta Environment Calculation Methods for Gases and Particulates**

(after Cheng et al., 2001)



## Variables

|                 |   |
|-----------------|---|
| PAI             | Potential Acid Input ( $\text{kg H}^+ \text{ha}^{-1} \text{yr}^{-1}$ )                                |
| [X]             | Concentration of X chemical species deposited ( $\text{kg ha}^{-1} \text{yr}^{-1}$ )                  |
| F               | Dry Deposition Flux ( $\mu\text{g m}^{-2}\text{s}^{-1}$ )   |
| $V_d$           | Deposition Velocity ( $\text{m s}^{-1}$ )   |
| C               | Concentration ( $\mu\text{g m}^{-3}$ )  |
| $R_a$           | Aerodynamic Resistance ( $\text{s m}^{-1}$ )  |
| $R_b$           | Boundary-Layer Resistance ( $\text{s m}^{-1}$ )   |
| $R_c$           | Surface Resistance ( $\text{s m}^{-1}$ )  |
| k               | von Karman constant (0.4)   |
| $u^*$           | Friction velocity ( $\text{m s}^{-1}$ )   |
| z               | Reference height (10 m)   |
| $z_0$           | Surface roughness length (m)  |
| $\psi$          | Integrated stability correction term  |
| L               | Monin-Obukhov length scale  |
| u               | Wind speed ( $\text{m s}^{-1}$ )  |
| $\sigma_\theta$ | Standard deviation of wind direction (radians)  |
| $R_i$           | Bulk Richardson number  |
| g               | Gravitational acceleration ( $9.81 \text{ m s}^{-2}$ )  |
| $T_d$           | Temperature difference between 10 and 2 m ( $T_{10} - T_2$ )  |
| $T_2$           | Temperature at 2 m (Kelvin)   |
| H               | Sensible heat flux  |
| B               | (see equation on page 50)   |
| $\eta$          | Dynamic viscosity of air ( $18.0 \times 10^{-6} \text{ N s m}^{-2}$ at 1 atm and $25^\circ\text{C}$ ) |
| $\rho$          | Density of air ( $1.18 \text{ kg m}^{-3}$ at 1 atm and $25^\circ\text{C}$ )                           |
| D               | Diffusion coefficient of the substance of interest ( $\text{cm}^2 \text{s}^{-1}$ )                    |
| Pr              | Prandtl number for air (0.72)   |
| $\eta/\rho D$   | Schmidt number  |
| RH              | Relative humidity   |
| SW              | Soil Wetness  |

## Equations:

$$\text{PAI}_{\text{dry}} = \frac{[\text{SO}_2]}{64} + \frac{[\text{NO}_2]}{46} + \frac{[\text{HNO}_2]}{47} + \frac{[\text{HNO}_3]}{63} + 2 \frac{[\text{SO}_4^{2-}]}{96} + \frac{[\text{NO}_3^-]}{62} + \frac{[\text{NH}_4^+]}{18}$$

deposition  
concentrations  
in  $\text{kg ha}^{-1} \text{y}^{-1}$

$$- \left( \frac{[K^+]}{39} + \frac{[Na^+]}{11} + 2 \frac{[Ca^{2+}]}{40} + 2 \frac{[Mg^{2+}]}{24} \right)$$

$$F = V_d C$$

$$V_d = \frac{1}{(R_a + R_b + R_c)}$$

### Summary of Species Specific Deposition Velocity Formulae:

$$V_{d(SO_2)} = \frac{1}{R_a + R_{b(SO_2)} + R_{c(SO_2)}}$$

$$V_{d(NO_2)} = \frac{1}{R_a + R_{b(NO_2)} + R_{c(NO_x)}}$$

$$V_{d(HNO_3)} = \frac{1}{R_a + R_{b(SO_2)}}$$

$$V_{d(HNO_2)} = \frac{1}{R_a + R_{b(HNO_2)}}$$

}  $R_c$  is treated as being negligible for nitric and nitrous acid.

$$V_{d(SO_4^{2-}, NH_4^+)} = \frac{1}{R_a + R_{b(SO_4^{2-})}}$$

$$V_{d(NO_3^-, Ca^{2+}, Mg^{2+}, K^+, Na^+)} = \frac{1}{R_a + (0.5 \times R_{b(SO_4^{2-})})}$$

### Aerodynamic Resistance ( $R_a$ ):

$$R_a = \frac{1}{ku^*} \left\{ \ln \frac{z}{z_0} - \psi \left( \frac{z}{L} \right) \right\} \quad (R_a \text{ is infinite and } V_d = 0 \text{ when } u \text{ and } T_d \text{ are zero})$$

$$u^* = \frac{u \sigma_\theta}{1.9} \quad (\text{this relationship is used as an initial estimate of } u^* \text{ to calculate } z_0, \text{ a more precise value of } u^* \text{ is calculated after } z_0 \text{ is obtained – refer to below})$$

$$z_0 = z e^{-\left(\frac{0.4u}{u^*}\right)} \quad (\text{calculated as a monthly average using data where the wind speed is } >6 \text{ m s}^{-1})$$

$$R_i = \frac{gzT_d}{T_2 u^2}$$



**A more precise value of  $u^*$  calculated after  $z_0$  is obtained (based on atmospheric conditions):**

$$\text{Stable conditions} \quad R_i > 0 \quad u^* = ku \left\{ \ln \left( \frac{z}{z_0} \right) (1 + 4.7 Ri) \right\}^{-1}$$

$$\text{Unstable conditions} \quad R_i < 0 \quad u^* = \frac{ku}{\ln \left( \frac{z}{z_0} \right) \sqrt{1 - \left\{ \frac{9.4 Ri}{1 + (7.4 B)} \right\}}}$$

$$\text{Neutral conditions} \quad R_i = 0 \quad u^* = \frac{ku}{\ln \left( \frac{z}{z_0} \right)}$$

**Calculation of  $\psi$  (based on atmospheric conditions):**

$$\text{Stable conditions} \quad \psi = -\frac{5z}{L} \quad \text{where } L = \frac{T_2 u^{*3}}{kHg}$$

$$\text{Unstable conditions} \quad \psi = 2 \ln \left\{ \frac{1}{2} \left( 1 + \sqrt{1 - \frac{15z}{L}} \right) \right\}$$

$$\text{Neutral conditions} \quad \psi = 0$$

**Calculation of  $H$  (based on atmospheric conditions):**

$$\text{Neutral and Stable conditions} \quad H = \left\{ \frac{uT_d}{0.74} \right\} \left\{ \frac{k}{\ln \left( \frac{z}{z_0} \right)} \right\}^2 \left\{ \frac{1}{(1 + 4.7 Ri)^2} \right\}$$

$$\text{Unstable conditions} \quad H = \left\{ \frac{uT_d}{0.74} \right\} \left\{ \frac{k}{\ln \left( \frac{z}{z_0} \right)} \right\}^2 \left\{ 1 - \frac{9.4 Ri}{(1 + 5.3 B)} \right\}$$

$$\text{where } \mathbf{B} = 9.4 \left[ \frac{k}{\ln\left(\frac{z}{z_0}\right)} \right]^2 \left[ \left| R_i \right| \frac{z}{z_0} \right]^{1/2}$$

### **Boundary Layer Resistance ( $R_b$ ):**

#### **$R_b$ (gases):**

$$R_b = R_b = \frac{2}{ku_*} \left( \frac{\eta}{\rho D} \times \frac{1}{Pr} \right)^{2/3}$$

$$R_b = \frac{7.22}{u_*} \text{ for SO}_2 \text{ and HNO}_3$$

$$R_b = \frac{6.18}{u_*} \text{ for NO}_2$$

$$R_b = \frac{6.09}{u_*} \text{ for HNO}_2$$

#### **$R_b$ (particulates):**

$R_b$  values for particulate sulphate are obtained from scientific literature for daytime and nighttime as a function of surface type and weighted according to average day length for each month at a mid-Alberta latitude location (54°N latitude) after Cheng and Angle (1993) as cited in Cheng et al. (2001).

Boundary-Layer Resistance ( $s \text{ cm}^{-1}$ ) for Particulate Sulphate, Day Length Weighted Averages at 54°N Latitude for the Middle of Each Month.

| Surface Type       | Winter<br>(Dec, Jan, Feb) |     | Spring<br>(Mar, Apr, May) |     | Summer<br>(Jun, July, Aug) |     | Autumn<br>(Sep, Oct, Nov) |     |
|--------------------|---------------------------|-----|---------------------------|-----|----------------------------|-----|---------------------------|-----|
|                    | Dry                       | Wet | Dry                       | Wet | Dry                        | Wet | Dry                       | Wet |
| Deciduous Forest   | 16.9                      | 0   | 5.4                       | 0   | 1.3                        | 0   | 3.2                       | 0   |
| Coniferous Forest  | 2.5                       | 0   | 2.7                       | 0   | 1.9                        | 0   | 2.3                       | 0   |
| Wetland/Swamp*     | 20.4                      | 0   | 3.8                       | 0   | 2.6                        | 0   | 3.2                       | 0   |
| Grassland*         | 20.4                      | 0   | 5.6                       | 0   | 3.9                        | 0   | 4.7                       | 0   |
| Cropland*          | 20.4                      | 0   | 9.0 <sup>†</sup>          | 0   | 3.9                        | 0   | 7.9 <sup>‡</sup>          | 0   |
| Urban <sup>§</sup> | 33.9                      | 0   | 10.9                      | 0   | 2.6                        | 0   | 6.3                       | 0   |
| Open Water         | 0                         | 0   | 0                         | 0   | 0                          | 0   | 0                         | 0   |
| Snow/Ice           | 20.4                      | 0   | -                         | -   | -                          | -   | -                         | -   |

\* in winter, wetland, grassland, and cropland treated as a snow surface.

<sup>†</sup> bare soil and active growth.

<sup>‡</sup> bare soil and senescent growth.

<sup>§</sup> consists of a mixture of deciduous forest and buildings.



$$\text{Day length Weighted Seasonal Average } R_b = \frac{\text{day length}}{24\text{hrs}} (R_{b \text{ day}}) + \left(1 - \frac{\text{day length}}{24\text{hrs}} (R_{b \text{ night}})\right)$$

$$\text{Day length} = 0.133 \left\{ \cos^{-1} \left( -\tan(55^\circ) \times \tan(\text{Solar Declination}) \right) \right\}$$

$$\text{Solar Declination} = 23.45 \left\{ \sin \left( \frac{360 \times (284 + \text{Julian Day})}{365} \right) \right\}$$

### Surface Resistance ( $R_c$ ):

Bulk surface resistance values are used from literature as a function of surface type, surface wetness, and incident radiation. Day length weighted average  $R_c$  values for  $\text{SO}_2$  and  $\text{NO}_2$  are used from Voldner et al (1986), Arritt et al (1987) and Walcek et al (1986) as cited in Cheng et al. (2001):

#### Day Length Weighted Averages Bulk Surface Resistance ( $\text{s cm}^{-1}$ ) for Sulphur Dioxide ( $\text{SO}_2$ ).

| Surface Type      | Winter<br>(Dec, Jan, Feb) |     | Spring<br>(Mar, Apr, May) |     | Summer<br>(Jun, July, Aug) |     | Autumn<br>(Sep, Oct, Nov) |     |
|-------------------|---------------------------|-----|---------------------------|-----|----------------------------|-----|---------------------------|-----|
|                   |                           |     |                           |     |                            |     |                           |     |
|                   | Dry                       | Wet | Dry                       | Wet | Dry                        | Wet | Dry                       | Wet |
| Deciduous Forest  | 10                        | 10  | 4.7                       | 0   | 3.5                        | 0   | 7.9                       | 0.4 |
| Coniferous Forest | 5                         | 5   | 4.1                       | 0   | 3.5                        | 0   | 4.9                       | 0.2 |
| Wetland/Swamp*    | 7                         | 1   | 0.5                       | 0   | 0.7                        | 0   | 1                         | 0.1 |
| Grassland*        | 7                         | 1   | 1                         | 0   | 1.3                        | 0   | 2                         | 0.1 |
| Cropland*         | 7                         | 1   | 0†                        | 0   | 2                          | 0   | 2‡                        | 0.1 |
| Urban§            | 10                        | 2   | 10                        | 0   | 10                         | 0   | 10                        | 0.1 |
| Open Water        | 0                         | 0   | 0                         | 0   | 0                          | 0   | 0                         | 0   |
| Snow/Ice          | 7                         | 1   | -                         | -   | -                          | -   | -                         | -   |

\* in winter, wetland, grassland, and cropland treated as a snow surface.

† bare soil and active growth.

‡ bare soil and senescent growth.

§ consists of a mixture of deciduous forest and buildings.

#### Day Length Weighted Averages Bulk Surface Resistance ( $\text{s cm}^{-1}$ ) for Nitrogen Dioxide ( $\text{NO}_2$ ).

| Surface Type      | Winter<br>(Dec, Jan, Feb) |      | Spring<br>(Mar, Apr, May) |      | Summer<br>(Jun, July, Aug) |      | Autumn<br>(Sep, Oct, Nov) |      |
|-------------------|---------------------------|------|---------------------------|------|----------------------------|------|---------------------------|------|
|                   |                           |      |                           |      |                            |      |                           |      |
|                   | Dry                       | Wet  | Dry                       | Wet  | Dry                        | Wet  | Dry                       | Wet  |
| Deciduous Forest  | 20.0                      | 70.0 | 3.3                       | 70.0 | 2.2                        | 70.0 | 4.7                       | 70.0 |
| Coniferous Forest | 10.0                      | 70.0 | 2.7                       | 70.0 | 2.2                        | 70.0 | 3.3                       | 70.0 |
| Wetland/Swamp*    | 50.0                      | 70.0 | 12.1                      | 70.0 | 11.5                       | 70.0 | 12.9                      | 70.0 |
| Grassland*        | 50.0                      | 70.0 | 3.3                       | 70.0 | 3.3                        | 70.0 | 6.6                       | 70.0 |
| Cropland*         | 50.0                      | 70.0 | 3.3†                      | 70.0 | 4.6                        | 70.0 | 7.9‡                      | 70.0 |
| Urban§            | 10.0                      | 70.0 | 10.0                      | 70.0 | 10.0                       | 70.0 | 10.0                      | 70.0 |
| Open Water        | 70.0                      | 70.0 | 70.0                      | 70.0 | 70.0                       | 70.0 | 70.0                      | 70.0 |
| Snow/Ice          | 50.0                      | 70.0 | -                         | -    | -                          | -    | -                         | -    |

\* in winter, wetland, grassland, and cropland treated as a snow surface.

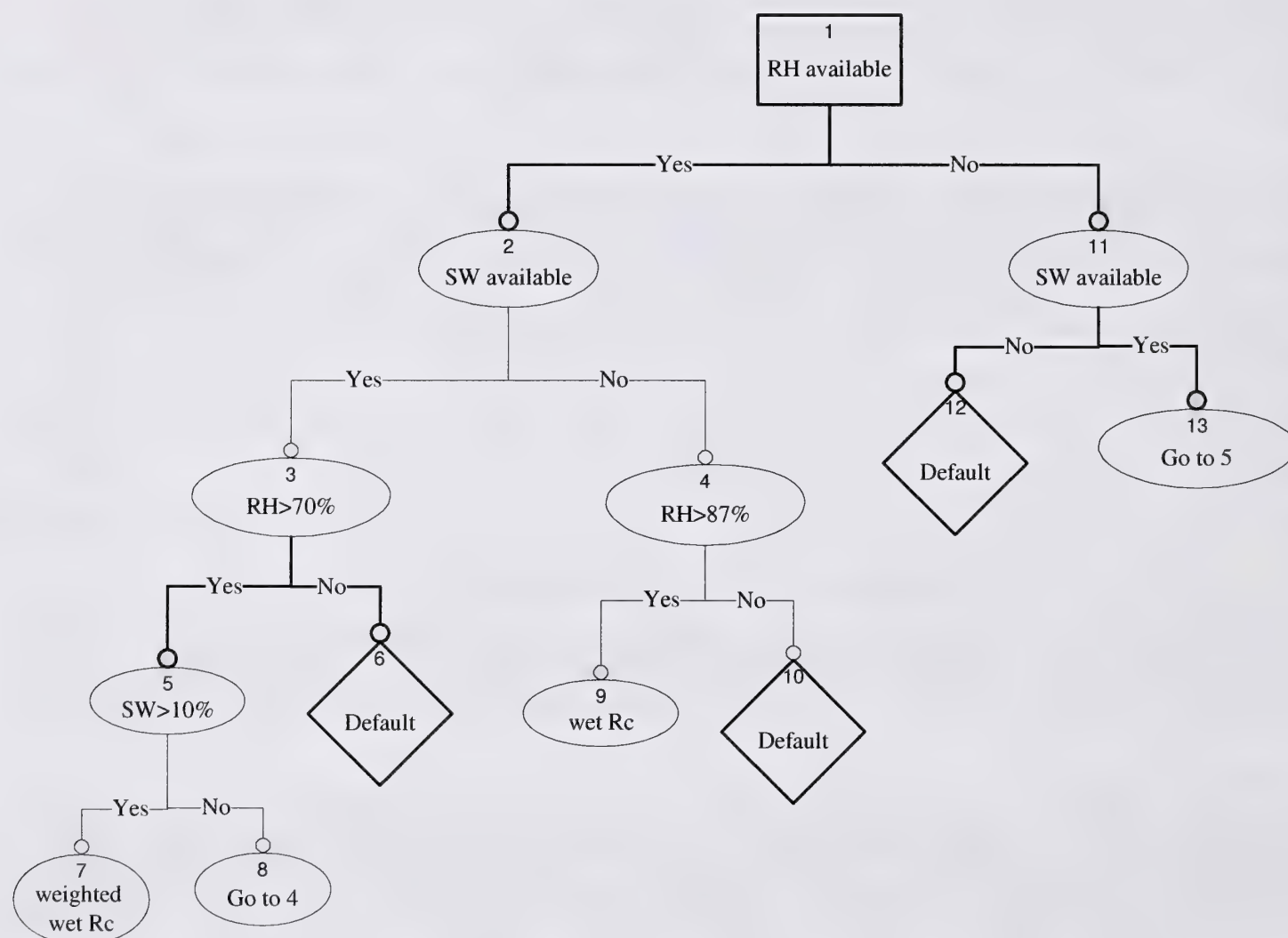
† bare soil and active growth.

‡ bare soil and senescent growth.

§ consists of a mixture of deciduous forest and buildings.

$R_c$  ( $\text{HNO}_3$ ):  $10 \text{ s m}^{-1}$  (for all seasons and all surfaces)  
 $R_c$  ( $\text{HNO}_2$ ):  $10 \text{ s m}^{-1}$  (for all seasons and all surfaces)  
 $R_c$  ( $\text{NH}_3$ ):  $28 \text{ s m}^{-1}$  (dry)  
 $9 \text{ s m}^{-1}$  (wet)  
 $201 \text{ s m}^{-1}$  (when  $T_2 < 0^\circ\text{C}$ )  
 $R_c$  (particulates):  $0 \text{ s m}^{-1}$

$R_c$  is calculated based on surface wetness criteria, such that it either represents a “total dry condition,” “total wet condition,” or “weighted wet condition” using the following flowchart, and relative humidity (RH) and surface wetness (SW) criteria:



Adapted from Bates (1996)

Default =  $R_c$  value for dry conditions

Wet  $R_c$  =  $R_c$  value for wet conditions

Weighted Wet  $R_c$  = Time weighted wet  $R_c$

$$\text{Time weighted wet } R_c = \left( \frac{SW}{100} \times \text{wet } R_c \right) + \left[ \left( 1 - \frac{SW}{100} \right) \times \text{dry } R_c \right]$$



### **Calculation of $V_d$ in the absence of meteorological data:**

Missing hourly meteorological data are treated in the following manner:

- 1 hour of meteorological data missing → the average resistance of the hours before and after are used to represent the missing hour
- consecutive hours of meteorological data missing → each hour's calculated median resistance for the month is used to represent the missing hours

## **APPENDIX II**

### **WBEA Dry Deposition Calculation Methods for Surface Resistance of Gases**



## **Surface Resistance ( $R_c$ ):**

Surface (canopy) resistance is based on a Leaf Area Index (LAI) approach. The LAI approach is based upon three main pathways for uptake/reaction of a pollutant within the vegetation or surface:

1. Transfer through the stomatal pore and dissolution or reaction in the mesophyll cells.
2. Reaction with or transfer through the leaf cuticle.
3. Transfer into the ground/water surface.

These pathways are treated as three resistances in parallel (Scire et al., 2000):

$$R_c = [LAI/r_f + LAI/r_{cut} + 1/r_g]^{-1}$$

where

$r_f$  = internal foliage resistance (s/m) (Pathway 1)

$r_{cut}$  = cuticle resistance (s/m) (Pathway 2)

$r_g$  = ground or water surface resistance (s/m) (Pathway 3)

LAI = leaf area index (ratio of leaf surface area divided by ground surface area) specified as a function of land use type (unitless)

The LAI is the upper side leaf area per unit area of soil below it. It is expressed as  $m^2$  leaf area per  $m^2$  ground area. The LAI is the index of the leaf area that actively contributes to surface heat and vapor transfer. It is generally the upper, sunlit portion of a dense canopy. LAI values for various types of vegetation can vary widely.

EPCM (2002) used default values for LAI at a dedicated acid deposition monitoring site (Fort McKay) – a high density coniferous forest. A LAI value of 7.0 was used for the growing (summer) season – May through September, while a winter value is estimated by EPCM (2002) to be 0.5 units lower – or 6.5.

## **Internal Foliage Resistance ( $r_f$ )**

The first pathway ( $r_f$ ) is usually the most important for uptake of soluble pollutants in vegetated areas. This pathway consists of two components:

$$r_f = r_s + r_m$$

where

$r_s$  = resistance to transport through the stomatal pore (s/m)

$r_m$  = resistance to dissolution or reaction of the pollutant in the mesophyll (spongy parenchyma) cells (s/m)

## **Stomatal Resistance ( $r_s$ )**

Stomatal action imposes a strong diurnal cycle on the stomatal resistance, and, due to its important role for gaseous, soluble pollutants such as SO<sub>2</sub>, on the deposition velocity. Stomatal opening/closing is a response to the plant's competing needs for uptake of CO<sub>2</sub> and prevention of water loss from the leaves. The stomatal resistance can be written (O'Dell et al., 1977 as cited in Scire et al., 2000) as:

$$r_s = p/(bD)$$

where

- $p$  = stomatal constant ( $\approx 2.3 \times 10^{-8} \text{ m}^2$ )  
 $b$  = width of the stomatal opening (m)  
 $D$  = molecular diffusivity of the pollutant ( $\text{m}^2/\text{s}$ )

The width of the stomatal opening is a function of the radiation intensity, moisture availability, and temperature. The variation of  $b$  during periods when vegetation is active can be represented as (Pleim et al., 1984 as cited in Scire et al., 2000):

$$b = b_{\max} [S/S_{\max}] + b_{\min}$$

where

- $b_{\max}$  = maximum width of the stomatal opening (m) ( $\approx 2.5 \times 10^{-6}$ ) (Padro et al., 1991 as cited in Scire et al., 2000)  
 $b_{\min}$  = minimum width of the stomatal opening (m) ( $\approx 2.5 \times 10^{-6}$ )  
 $S$  = solar radiation received at the ground ( $\text{W}/\text{m}^2$ )  
 $S_{\max}$  = solar radiation at which full opening of the stomata occur ( $\text{W}/\text{m}^2$ )

During periods of moisture stress, the need to prevent moisture loss becomes critical, and the stomata close. It can be assumed that  $b = b_{\min}$  for unirrigated vegetation under moisture stress conditions. The effect of temperature on stomatal activity has been reviewed by Pleim et al. (1984) as cited in Scire et al. (2000). The most significant effects are due to temperature extremes. During cold periods ( $T < 10^\circ\text{C}$ ), metabolic activity slows, and  $b = b_{\min}$ .

### **Mesophyll Resistance ( $r_m$ )**

The mesophyll resistance ( $r_m$ ) depends on the solubility and reactivity of the pollutant. It is an input parameter supplied to the deposition model for each gaseous species. O'Dell et al. (1977) as cited in Scire et al. (2000) estimated the mesophyll resistance for several pollutants. For soluble pollutants such as SO<sub>2</sub> and NH<sub>3</sub>,  $r_m \approx 0$ . The mesophyll resistance can be large for less soluble pollutants such as NO<sub>2</sub> ( $\approx 50,000 \text{ s/m}$ ) and NO ( $\approx 940,000 \text{ s/m}$ ). For other pollutants,  $r_m$  can be estimated based on the solubility and reactivity characteristics of the pollutant.

### **Cuticle Resistance( $r_{\text{cut}}$ )**

The second pathway for deposition of gases in the vegetation layer is via the leaf cuticle. This includes potential direct passage through the cuticle or reaction of the pollutant on the cuticle surface. Hosker and Lindberg (1982) as cited in Scire et al. (2000) suggest that passage of gases



through the cuticle is negligible. Therefore, cuticle deposition is likely to be controlled by the pollutant reactivity. Pleim et al. (1984) as cited in Scire et al. (2000) parameterize  $r_{cut}$  as a function of the pollutant reactivity of the depositing gas relative to the reference values for  $SO_2$ :

$$r_{cut} = \frac{A_{SO_2}}{A} r_{cut}(SO_2)$$

where

$A_{SO_2}$  = reactivity of  $SO_2$  ( $\approx 8.0$ ) reactivity

$A$  = parameter for the depositing gas

$R_{cut}(SO_2)$  = empirically determined cuticle resistance of  $SO_2$  (s/m)

Padro et al. (1991) as cited in Scire et al. (2000) suggest  $r_{cut}(SO_2) \approx 3,000$  s/m. Reactivity values for other pollutants are estimated at 8.0 ( $NO_2$ ), 15.0 ( $O_3$ ), and 18.0 ( $HNO_3$ ).

### Ground/Water Resistance ( $r_g$ )

The third pathway through the “vegetation layer” ( $r_g$ ) does not involve vegetation. It is deposition directly to the ground or water surface. In moderately or heavily vegetated areas, the internal foliage and cuticle resistances usually control the total canopy resistance and  $r_g$  can be ignored. However in sparsely vegetated areas, deposition directly to the surface may be an important pathway. Over water, deposition of soluble pollutants can be quite rapid. Ground resistance,  $r_g$ , over land surfaces can be expressed relative to a reference value for  $SO_2$  (Pleim et al., 1984 as cited in Scire et al., 2000):

$$r_g = \frac{A_{SO_2}}{A} r_g(SO_2)$$

$r_g(SO_2)$  = ground resistance of  $SO_2$  ( $\approx 1,000$  s/m) (Padro et al., 1991 as cited in Scire et al., 2000)









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